# INDUSTRIAL ORGANIC ANALYSIS

FOR THE USE OF TECHNICAL AND ANALYTICAL CHEMISTS AND STUDENTS

BY

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WITH A FOREWORD

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# FOREWORD

BY PROFESSOR J. C. IRVINE, D.SC., PH.D.

THE relationship between science and industry has been the subject of endless discussion in recent years, and, if tangible results have not been numerous, signs are not wanting that the value of scientifically trained men in industry is now frankly recognised in some quarters and that the universities and colleges are anxious to provide for any demand for such men which may arise.

So far there is agreement between the parties, but, assuming that the employer is perfectly clear as to what he wants, teaching institutions are by no means agreed on the best means of modifying their curricula to meet modern requirements. The orthodox course for a degree in science certainly shows a desirable uniformity, but differences of opinion at once arise when attempts are made to frame an educational policy which will retain for institutions of university rank the ideal of wide culture, while admitting some aspect of practical training of use in the field of industrial work.

In the particular case of chemical training, these difficulties are modified, if not entirely removed, when the special qualifications desirable in the technical chemist are taken into account. That he should have received as thorough a training as possible in what is often termed "Pure Chemistry" may be accepted as a matter of course. It is equally essential that the student should be trained to think scientifically, and that his

capacity for original inquiry should be developed. Such a result may be achieved in particular instances through the inspiration of a gifted teacher, but the best route to this desirable end is found in a course of original research undertaken after graduation or its equivalent.

It may be admitted that the young graduate is frequently of little immediate value to the manufacturer. It is equally true that he has to be trained, often slowly and laboriously, in the methods and spirit of research, but it is at once the privilege and duty of the university or college to supply this training. After two (or it may be three) years spent at this work the latent initiative and resource of the student are brought into operation, and his capacities for useful employment are thereby increased enormously. In the absence of any definite experience in technical methods, however, these powers will not be developed to their fullest advantage. Strictly speaking, a course of specialised technical work should follow at this stage, but the obstacles in the way are manifold. Our student is now probably between twenty-four and twenty-five years of age, and is naturally anxious to begin his life's work. Unless he has good prospects of obtaining a position in some particular industry, he is hardly justified in making a choice of any one branch of Applied Chemistry for special study. Obviously in the course of training here outlined, the shortest possible route to technical experience has to be taken.

In most teaching institutions, little or no provision is made for instruction in Applied Chemistry, or in the technique of Commercial Analysis as a course to be taken only after scientific Chemistry has been absorbed by study and expanded by research. We have the university-trained chemist and the technical chemist,

the former with a slender idea of the world of manufacture, and the latter often lacking the mental discipline of pure research, and each type of man requires something more before he can be really useful.

Mr. Arup's book is an attempt to supply the deficiency of one of the above types. He has provided a course of technical organic analysis which can be profitably undertaken either by the undergraduate or by the more mature original worker. The author has directed his attention to modern standard methods which apply to important substances, and the best type of student who works through a selection of the exercises should get into touch with technical methods and the literature of commercial processes. Whatever business instincts he may have will be aroused, and some definite form and direction conveyed to his efforts to obtain a suitable post.

A comparatively small amount of preliminary technical training can often transform the research chemist into a valuable official in a business concern or factory, but some beginning must be found for this transformation. As Professor Martin Bogert has recently said,* "the really important thing is to bring together the problem and the man competent to solve it," and although no laboratory course can take the place of factory experience, the training embodied in Mr. Arup's book may help many young chemists to offer themselves for technical posts with some knowledge of how to begin their work, and some ideas regarding its possible developments.

Apart from its effect on the student, there is one other aspect of the training indicated in this book, and that is

* Presidential Address to the Society of Chemical Industry, 1913.

its influence on the teacher of Chemistry. In the address already quoted, Professor Bogert emphasises this point and states that if the teacher were more familiar with industrial problems he would often select topics for his research students bearing on these subjects. The adoption of such a policy would in no way endanger the progress of scientific Chemistry in face of the fact that the large majority of students of Chemistry, who must inevitably qualify themselves for technical posts, would in the natural course of events carry out some strictly scientific research as a preliminary to technical investigation.

Mr. Arup's book is a practical contribution to a problem which becomes more urgent every day.

J. C. IRVINE.

THE UNIVERSITY,
ST. ANDREWS,
1913.

# PREFACE

THIS volume has been written for the use of students who, having received a thorough training in theoretical and practical Chemistry, may desire to gain some insight into the methods and principles of industrial organic analysis, and as a work of reference for chemists engaged in technical or analytical work.

Considering that the great majority of students who specialise in Chemistry sooner or later take up industrial work, the Author considered that some attempt might be made towards bridging the gap which undoubtedly exists between academic and scientific Chemistry, on the one hand, and industrial Chemistry on the other. With this motive, he has written the present work, endeavouring to treat the subject in such a way that it may prove of interest from the scientific, industrial and educative points of view.

It may be pointed out at once that the subject-matter of this volume is not intended to replace any portion of the ordinary curriculum or the research training which forms so valuable a feature in the educational programmes of many of our colleges and universities; it is recognised that the academic training of the industrial chemist should be as thorough and comprehensive as possible, in order that he may be able to take a broad view of the many different problems which may confront him in practice; it was, however, thought that the present system of training might well be supplemented by showing the student how his theoretical knowledge

can be applied in industrial Chemistry, at any rate, as far as his laboratory work is concerned.

There is no doubt that the student just entering on industrial work has much to learn, and that his success will generally depend on the quickness and efficiency with which he applies his knowledge to the solving of the problems with which he has to deal; the object aimed at here is to help to give the student some opportunity of putting himself into touch with the requirements of an important branch of his new work, and at the same time, it is hoped that something may be done towards modifying the somewhat sceptical attitude sometimes taken by the manufacturer towards the scientifically trained man or rather, the student fresh from college.

Regarding the scope of this work, it may be said that only such sections of the subject as seemed to be of sufficient general interest have been chosen. More attention has been paid to natural products and substances obtained from these by comparatively simple means than to products which are obtained by complex manufacturing operations. The object has not been to teach certain methods of analysis connected with specific manufacturing operations, but rather to initiate the student into the general methods and spirit of industrial organic analysis. He may thus learn to cope with more complex problems in this field of work with the aid of the standard works of reference.

Regarding the choice of analytical methods, the Author has selected standard well-tried processes, especially those which are instructive in throwing light on the characteristic chemical behaviour of the substances under examination. Methods requiring the use of special apparatus such as, for example, the refracto-

meter or coal calorimeter, not usually to be found in the ordinary teaching laboratory, have not been described in detail; through the references given both in the text and at the end of each chapter, however, the reader will readily find any such methods fully described.

More complete working details have sometimes been given than would be required by the expert analyst, though, on the other hand, it has not been thought necessary to describe in detail such well-known analytical operations as may be found fully described in most text books on organic and inorganic analysis.

Stress has been laid on the reasons for which every analytical operation is carried out, as well as on the discussion of the practical significance of the results obtained. In this way, it is hoped that the work may prove interesting to students and, at the same time, impress them with some of the most important aspects of industrial analysis.

Frequent references have been made to standard works of reference when the subject passes beyond the scope of the work, and it is hoped that the bibliography appended to each chapter may prove a useful addition to the text. To these works the Author desires to express his indebtedness for much of the material contained in this volume, and he also wishes to thank Professor J. C. Irvine, of the University of St. Andrews, for valuable suggestions received in the course of its preparation.

The Author's thanks are further due to Mr. W. A. Davis, of the Rothamsted Experimental Station, and Mr. S. H. Blichfeldt, chief chemist and bacteriologist to Messrs. Otto Monsted, Ltd., for useful information concerning analytical methods, and to Mr. R. E.

Doolittle, of the New York Foods and Drugs Section Laboratory, for his courtesy in supplying information concerning the law in America regarding preservatives in foods.

PAUL S. ARUP.

SOUTHALL,
1913

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# INDUSTRIAL ORGANIC ANALYSIS

## INTRODUCTION.

This chapter contains some general remarks on the work to be described, and suggestions for the use of this volume.

*Sampling.*—A few words may first be said concerning the operation of taking the sample for analysis. Although the student may not, in the ordinary course of events, have many opportunities of taking his own samples direct from large masses of material, yet he should never lose sight of the importance of always working on a fair average sample of the consignment or batch of material to be valuated or tested by chemical and physical examination. It is obvious that if the sample for analysis has been picked by a prejudiced person, or carelessly taken, the analytical results obtained may, in many cases, fall far short of representing the average properties or composition of the bulk of the material; and the analysis, however carefully and efficiently it may have been carried out, may be practically valueless, at any rate to the person who would be most directly interested in obtaining reliable information as to the quality of the material.

If unable to sample from the bulk, the student should, at all events, always make a point of taking a genuine

average sample for analysis from the material supplied to him; he should mention in his report the weight or bulk of the sample received for analysis, the date received in the laboratory, the date analysed, and as far as is known to him, the age and previous history of the sample on receipt. The latter points are mainly of importance when dealing with materials which are liable to decomposition on keeping.

The method of sampling will naturally depend on the nature of the substance dealt with. An example of a method for sampling solid substances is given in Chapter I. (Sampling of Coal); the details given will serve as an illustration of the methods which may be employed for the sampling of hard solids, though various modifications may naturally suggest themselves when dealing with other materials of a similar nature. Soft or semi-solid material, such as butter, soap, solid fats, anthracene, etc., may be sampled by means of the auger-shaped instrument described in Chapter VI., p. 227, several samples being taken in different directions from the barrel, drum or box, and, if possible, melted together, the analytical sample being taken from the well-mixed, molten material; an example of this method is given in Chapter VI. (Sampling of Butter). This method of melting together several samples taken from the bulk should always be adopted if the material can be melted at a conveniently low temperature, and without decomposition or loss of volatile constituents. The sampling of liquids usually presents the least difficulty, though care should always be taken that any sediment or immiscible liquid which may be present be stirred into the mass before taking the sample. (See Chapter VI., p. 190.)

*Accuracy of Results.*—Many of the analytical pro-

cesses described are only intended to yield results accurate to two, or, at the most, three figures, as in industrial work extreme accuracy may often be sacrificed with advantage for rapidity and ease in working. In many cases, indeed, highly exact methods of analysis, even if available, would be too lengthy and complicated for frequent use in the technical laboratory, while very little would be gained by obtaining results correct to more than, say, one-tenth, or even 1 per cent. For these reasons, time may often be saved by carrying out weighings on a balance weighing correctly to the nearest 5 or 10 milligrams, instead of on the accurate analytical balance, while approximate volumetric methods may often be made to take the place of the more exact gravimetric methods. Even in fairly accurate work, the rough balance may be used when weighing comparatively large quantities, say over 10 grams of material.

The student will learn to appreciate the relative accuracy aimed at in the various processes described, and to modify his methods of working accordingly; for example, in an operation such as the determination of the iodine value of fats, where scientifically accurate results are desirable, and the amount of material weighed is small, it will be necessary to use the accurate analytical balance. On the other hand, in operations such as the distillation tests for coal tar and petroleum or similar products, the material and its distillation fractions may be measured with sufficient accuracy by means of graduated cylinders, as the methods of analysis employed in such cases are only capable of yielding approximately accurate results. To sum up, the degree of accuracy required in the purely quantitative operations will depend, firstly, on the degree of accuracy of the results which the method is capable of yielding, and secondly, on

the amount of material dealt with; in this connection, however, it may be pointed out that although a method of analysis may only be capable of yielding approximate results, it may still be of the greatest importance to adhere closely to the prescribed experimental conditions in carrying it out.

The results of an analysis should never be expressed as being accurate to a greater degree than is warranted by the methods by which they have been obtained; thus in some cases it is well to express percentages of constituents as falling within fairly wide limits (see, for example, the estimation of cotton seed oil in arachis oil (Chapter III., p. 110)).

*Recording of Work and Reporting of Results.*—The usual notebook account should include not only a record of work done and observations made in its course, but also reasons for undertaking each operation described, explanations of all observations of interest, conclusions to be drawn from such observations and the analytical results, and explanations for all conclusions drawn. In addition to such an account, which will deal chiefly with the scientific aspect of the work, and may be regarded mainly as a private record for future guidance, it is suggested that the student should endeavour to write reports dealing primarily with the purely technical or commercial aspect of the results obtained. Such reports should be written so as to be perfectly intelligible to persons having little or no theoretical knowledge of Physics or Chemistry; they should be brief and logical, containing no statements which cannot easily be justified. Doubtful or speculative conclusions should either be omitted, or, at any rate, definitely characterised as such. Although technical terms cannot well be entirely avoided, the meaning of such terms as might be unfamiliar to the

person to whom the report is addressed, together with their qualitative or quantitative significance, should be clearly and briefly explained in the discussion of results. Any such explanations should be based mainly on observed or known facts, chosen and stated so as to corroborate the conclusions drawn from the results of the investigation; they should be in plain language, and as free as possible from theoretical explanations.

The report should commence with the particulars relating to the sample or samples, referred to above. Next, note may be made of any obvious properties of the samples, such as colour, smell, taste, consistency, etc., which may appear to be of interest. The results of the investigation may now be stated, after which will follow a brief discussion of the technical or commercial significance of the analytical results and other observations of interest, and finally the conclusions which may be drawn as to the technical or commercial value of the samples.

*Suggestions for the Use of this Volume.*—It is hardly expected that the student will find time to work through all the examples given in this volume; a selection may be made, partly according to the individual interest of the student, and partly with the object of obtaining experience of as many different types of analytical methods as possible.

It is suggested that the material for examination should generally be selected or prepared by the teacher, especially when the problem is to detect impurities or adulterants. In such cases it may often be advisable for the teacher to prepare samples containing known amounts of impurities or adulterants from genuine products, and to give the student an opportunity of making parallel tests or analyses on material which is known to be genuine and unadulterated; for example,

two samples may be supplied, with the information that one of them is suspected to be adulterated, the problem being to detect whether this be the case, and if so, the nature and approximate extent of the adulteration, as far as can be ascertained by the methods available to the student. In this way, the student will be able to test thoroughly the methods which he employs, and to form an opinion as to their relative value, and the significance of the results obtained by their means. This method of making parallel tests on perfectly genuine material should always be employed in trying new methods, or in doubtful cases. In preparing adulterated material for analysis, the foreign constituents should be added in such amounts as may be detected without great difficulty by the methods available to the student, as the object is rather to give him an opportunity of familiarising himself with the methods and principles of industrial analysis than to test his skill as an analyst by confronting him with problems which might even tax the resources of the expert.

Another form of problem which may be presented to the student is to supply him with a sample of material for examination, and to ask him either to report generally on its technical or commercial value, or to report on its value for some particular purpose; a problem of this nature may admit of wider possibilities than that indicated above, which simply demands the detection of certain foreign materials. It may also require more extensive inspection of standard works of reference on the subjects under investigation, and is at all times a test of the student's business capacities.

(All temperatures are given in degrees Centigrade, and all polarimetric readings in angular degrees, except where otherwise indicated.)

# CHAPTER I

## COAL AND COKE

### Introductory.

Coal, which is at present the most important of the sources of energy available for industrial purposes, has resulted from the mineralisation of the wood of prehistoric plants, which has remained buried in the crust of the earth, and undergone changes as the result of which it has more or less completely lost its organic nature. In availing ourselves of the latent energy stored up in the coal, by burning it in our grates and furnaces, we are, broadly speaking, reversing the processes by which the plant made use of the radiant energy of the sun in carrying out the endothermic changes necessary to convert water, carbonic acid and simple mineral substances into complex vegetable tissues. In view of the complex nature of the process of mineralisation of wood, which has resulted in the formation of coal, as well as the difference in the conditions under which it must have taken place in different localities, it is hardly surprising that we should meet with an almost endless variety of coals, passing by almost imperceptible gradations, from the comparatively soft brown coals, or lignites, which have still preserved the fibrous structure of the wood, to the hard, black, shiny anthracites, which show conchoidal fracture, and display but little evidence of their organic origin.

*Composition and Classification of Coals.*—The chief uses of coal are as follows: (1) steam raising; (2) household use; (3) metallurgical and other manufacturing operations, and for smiths' forges; (4) the production of coke, gas, tar and ammonia.

Coals are broadly classified according to their technical applications, which may be determined from the results of chemical and physical examination. The interpretation of the results of a chemical analysis of coal generally falls under two headings. Firstly, there are to be considered such constituents as water, sulphur and mineral matter, which must be regarded as more or less adventitious impurities, and which dilute the coal, reduce its calorific value or, if present in considerable amounts, may render it unsuitable for certain purposes. Secondly, the results of an analysis enable one to classify the coal, and to determine approximately the uses for which it is best suited. The soundest method for the classification of coals according to their chemical composition has been shown to be that which is primarily based on the percentages of carbon and hydrogen calculated on the coal, less water, sulphur and ash; thus, if S = the sum of the percentages of the water, sulphur and ash found in the coal, and C = the percentage of carbon found in the coal, then the percentage of carbon on the coal, less water, sulphur and ash, will be given by

$$C \frac{\cdot 100}{100 - S}$$

The reason for eliminating these constituents from the calculation is that they may vary considerably in amount in coals of essentially the same type, and thus affect the percentages of carbon and hydrogen, as determined on the coal itself, to such an extent that no true comparison can be made.

The accompanying table shows how coals are broadly classified into five main groups, on this basis. The lignites and the true anthracites are omitted from the scheme.

Apart from the content of more or less adventitious impurities, such as water, sulphur and ash, the main points which come into consideration in judging of the value of a coal for any particular purpose are as follows:—

The amount of gas and other volatile combustible matter formed on heating; this determines the

| Group | Per cent. on coal less Sulphur and Ash. | | | Percentage yield of Coke. | Character of Coke. | Sp. gr. of Coal. | Calorific Value of Coal in Calories. |
|---|---|---|---|---|---|---|---|
| | Carbon. | Hydrogen. | Oxygen | | | | |
| 1 | 75—80 | 5·5—4·5 | 19·5—15 | 50—60 | Pulverulent or slightly sintered. | 1·25 | 8,000—8,500 |
| 2 | 80—85 | 5·8—5·0 | 14·2—10 | 60—68 | Intumesced; semi-fused. | 1·28—1·30 | 8,500—8,800 |
| 3 | 84—89 | 5·5—5·0 | 11—5·5 | 68—74 | Coherent and fairly dense. | 1·30 | 8,800—9,300 |
| 4 | 88—91 | 5·5—4·5 | 6·5—5·5 | 74—82 | Coherent and very dense. | 1·30—1·35 | 9,300—9,600 |
| 5 | 90—93 | 4·5—4·0 | 5·5—3·0 | 82—90 | Pulverulent or slightly sintered. | 1·33—1·40 | 9,000—9,500 |

suitability of the coal for gas or tar manufacture, and the length of flame on combustion. The semi-anthracitic and anthracitic coals, which burn either with a short flame or practically no flame at all (Groups 4 and 5 in the above table), are more difficult to kindle than the long flame coals, but give a more intense heat, and produce little or no smoke. In these groups are included the well-known Welsh steam coals which are so largely used with marine boilers. Their freedom from smoke also renders them suitable for drying and curing hops and malt, and for horticultural purposes. Generally speaking, there is a direct relationship between the percentage of hydrogen and the length of flame, which both decrease in passing from Group 2 to Group 5.

Some coals (Groups 2, 3 and 4) become fused or semi-fused on heating or burning; these are referred to as caking coals. The non-caking coals, which are included in Groups 1 and 5, do not soften in this way, so that the individual lumps remain separate during combustion and provide for a freer access of air than do the caking coals. These peculiarities, as well as the relative length of the flame, must be taken into account in considering the type of furnace for which the coal is best suited. The caking power also influences the nature of the coke; thus, it will be noticed that the non-caking coals of Groups 1 and 5 produce pulverulent cokes, while those of Groups 2, 3 and 4 all produce more or less coherent cokes. The condition of the coke is further affected by the amount of gas formed on heating or combustion, which, generally speaking, varies directly with the percentage of hydrogen. We accordingly find that in passing from Group 2 to Group 4, the coke becomes denser and less porous.

The non-caking coals of Group 1 differ from those of Group 5 in burning with a long flame. They are mainly used for steam raising and are also suitable for gas making in some cases.

The coals belonging to Groups 2 and 3 are sometimes referred to as the "bituminous coals," though it should be understood that they have no connection with the substance known as bitumen. The softer varieties,

which are rich in volatile matter, are included in Group 2, and are usually known as the cannel coals; they are generally used for making gas, tar and ammonia. The coals of Group 3, which yield more coke than those of the former group, are used in smiths' forges and for manufacturing coke. Gas, tar and ammonia are sometimes also obtained from these coals.

The true anthracites and the lignites, which have not been dealt with hitherto, take their places at either end of the scale in the above classification. The former contain, as a rule, over 93 per cent. of carbon, and less hydrogen than the anthracitic coals belonging to Group 5; they burn without flame, are shiny jet-black in appearance, show conchoidal fracture, and sometimes have a specific gravity as high as 1·6. The lignites, on the other hand, contain less carbon and more hydrogen than the coals of Group 1; they are brownish-black in appearance, comparatively soft, and show a fibrous structure; owing to the relatively large amount of water and mineral matter which they contain, they have a lower calorific value than the true coals. Commercially they are of considerably less importance than the latter.

The relations between the chemical composition of coals and their chief properties and uses will be treated of in greater detail when the methods for determining the various constituents are described.

The above classification, and the explanatory remarks which follow it, must not be interpreted in too literal a sense; it is very difficult to place all coals in clearly defined groups forming a simple system of classification, while their uses, though primarily dependent on their chemical composition, must, in many cases, largely be determined by commercial considerations, such as the cost of the coal itself, cost of transport, and the value of the products obtainable from it (*i.e.*, gas, tar, ammonia or coke), which latter can only be satisfactorily determined by trials on a manufacturing scale. It is, however, generally possible to form an idea of the uses to which a coal may be put with greatest advantage from the results of a chemical examination; and moreover, if a

certain kind of coal has been found to be suitable for a certain purpose, chemical examination will show whether subsequent supplies are likely to fulfil the same conditions as the original sample. Again, it will always be useful to have a check on the water, ash and sulphur, which, if present in large amounts, invariably reduce the value of the coal as fuel. It should always be borne in mind that no analysis of coal will be of much value unless carried out on a fair average sample. (See below under "Sampling.")

The accompanying table (p. 14) shows the results of analyses, collected from various sources (most from "Analyses of British Coals and Cokes"), of typical coals and cokes, and their principal uses; together with the classification and explanatory remarks given above, it may be used as a guide for interpreting the results obtained by the analytical methods described below.

## Chemical Examination of Coal and Coke

*Sampling.*—In all technical and commercial analytical work, the operation of taking the sample for analysis is of the utmost importance; in the case of coal and coke, where such large masses are dealt with, this remark applies with especial force; it is obvious that a carefully picked sample may differ very considerably in composition from a sample which has been taken systematically and without prejudice, with the object of ascertaining, as far as possible, the average composition of the entire mass. Although the sampling of coal and coke can hardly be described as a laboratory operation, directions for systematic sampling are given here, owing to the extreme importance of this operation to the analyst. Whether or not the student has had the opportunity of taking his sample from a large mass of material, he should, at all events, follow out the latter part of the following directions in dealing with the reduced sample.

Quantities of coal or coke, as the case may be, amounting in all to 2 to 3 cwts., are taken at equal intervals

during unloading, or from all sides as well as the interior of the heaps, and removed to a place where the material will be protected from rain, dampness or direct sunlight. The whole is broken up into pieces about the size of apples, well mixed and arranged in the form of a square layer about 20 cm. deep. Diagonals are marked out on this square, and the material in two opposite triangles is removed; the remainder is then rearranged into a square, and the process repeated until about 200 lbs. remain, which are broken into pieces about the size of nuts, and systematically reduced, by the process just described, to about 10 lbs. The sample thus obtained is preserved in air-tight metal boxes till required for use, when it is further reduced as follows:—The whole is well mixed, whereupon 500 grams are abstracted in such a way as to obtain an average sample, and reduced to a fine powder, preferably in a small hand mill, so constructed as to avoid loss of dust during the grinding. The powder is placed in a dry bottle provided with a well-fitting glass stopper, and thoroughly mixed by shaking. Samples for analysis are taken from this bottle as required.

*Hygroscopic Water.* (*a*) *In Coal.*—2 to 4 grams of the powdered coal are weighed between a pair of well-ground watch glasses, so that moisture shall not be attracted through undue exposure to the air, and dried at a temperature of 105° on the shelf of an air oven, till constant in weight; the time required is usually about two hours. Overheating of the sample must be avoided, or appreciable quantities of volatile matter other than water may be lost; the process is always liable to a certain error due to the cause just mentioned, as well as oxidation of the coal, which occurs to a slight extent when the latter is heated in contact with air to the

| Description of Coal or Coke. | Carbon, per cent. | Hydrogen, per cent. | Oxygen, per cent. | Nitrogen, per cent. | Sulphur, per cent. | Ash, per cent. | Water, per cent. | Volatile Combustible Matter, excluding water, per cent. | Coke, less ash, per cent. | Percentage Composition, excluding Sulphur, Ash and Water. | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Carbon. | Hydrogen. |
| Anthracite, Pennsylvania . | 90·5 | 2·4 | 2·5 | *Nil* | *Nil* | 4·7 | *Nil* | — | — | 94·9 | 2·5 |
| Anthracite, S. Wales . . | 90·4 | 3·3 | 3·0 | 0·8 | 0·9 | 1·6 | 2·0 | — | — | 93·5 | 3·4 |
| Welsh steam coal (T. Hughes). | 87·7 | 4·0 | 2·2 | 1·0 | 1·0 | 2·8 | 1·3 | 8·0 [1] | 87·0 | 92·4 | 4·3 |
| Steam, manufacturing and house coal, Leicester . . | 74·9 | 4·5 | 15·0 | 1·2 | 0·9 | 3·0 | 13·2 | 30·0 | 54·2 | 90·4 | 6·0 |
| Coking coal, Durham (J. Pattinson) . . . | 83·84 | 4·7 | 3·8 | 1·3 | 0·8 | 4·2 | 1·3 | 22·7 | 71·8 | 89·5 | 5·1 |
| Steam, manufacturing, coking and house coal, Lancashire . | 81·7 | 5·0 | 5·8 | 1·9 | 0·5 | 2·9 | 2·4 | 20·7 | 77·9 | 86·6 | 5·3 |
| Gas coal, Durham . . . | 84·5 | 5·2 | 3·9 | 1·6 | 1·3 | 2·3 | 1·2 | 29·1 | 67·4 | 88·7 | 5·4 |
| Gas coal, Durham (J. Pattinson) | 82·4 | 5·1 | 6·6 | 1·1 | 0·9 | 2·0 | 2·0 | 31·3 | 64·7 | 86·6 | 5·4 |
| Steam coal, Durham . . | 81·2 | 5·2 | 6·2 | — | 0·9 | 2·2 | 2·1 | 31·9 | 63·8 | 86·3 | 5·5 |
| Gas coal, Commentry, France (Mahler) . . . . | 80·2 | 5·3 | 7·2 | 1·0 | — | 3·4 | 3·0 | 34·4 [2] | — | 85·7 [3] | 5·6 [3] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Steam coal, Blauzy, France (Mahler) . . . . | 79·4 | 5·0 | 8·7 | 1·1 | — | 1·9 | 3·9 | 31·9 [2] | — | 84·6 [3] | 5·3 [3] |
| House gas and manufacturing coal, Derbyshire . . | 68·0 | 4·5 | 10·2 | 1·2 | 0·6 | 3·8 | 11·8 | 32·7 | 50·7 | 81·1 | 5·3 |
| Steam coal, Staffordshire . | 78·6 | 5·3 | 12·9 | 1·8 | 0·4 | 1·0 | 1·1 | — | — | 79·7 | 5·4 |
| Cannel coal for gas and tar, Boghead . . . . | 65·3 | 9·1 | 5·4 | 0·7 | 0·1 | 18·6 | 0·5 | — | — | 80·8 | 11 2 |
| Malting coke, Alloa, Scotland (J. W. Napier) . . . | 94·8 | — | — | — | 0·5 | 4·7 | 0·1 | | | | |
| Coke (R. Tatlock and Thomson) | 90·4 | — | — | — | 1·2 | 7·1 | 0·3 | 1·0 | | | |
| Coke (McCreath) . . . | 89·6 [4] | — | — | — | 0·8 | 9·1 | 0·03 | 0·5 | | | |
| Coke, Connelsville, U.S.A. . | 87·5 [4] | — | — | — | 0·7 | 11·3 | 0·5 | 0·01 | | | |

[1] Volatile matter, excluding water and sulphur.

[2] Volatile matter calculated on coal, less ash and water.

[3] Carbon and hydrogen calculated on coal, less ash and water.

[4] Non-volatile carbon.

temperature employed for expelling the water. In most cases, however, the results thus obtained will be found to be sufficiently accurate for industrial purposes, though if the sample is subsequently to be analysed for hydrogen, it is advisable to employ a more accurate method, for errors in the figure for water as moisture will affect the figure for hydrogen as determined by combustion.

Where greater accuracy is desired, the water as moisture should be determined as follows :—2 to 4 grams of powdered coal are spread in a thin layer on a clock glass and placed over sulphuric acid in a vacuum desiccator which is then evacuated. The sample is weighed every 24 hours till no further loss in weight takes place ; before and during the weighing, the coal should be covered by a clock glass and exposed to the air as little as possible. If a good vacuum is maintained in the desiccator, the drying should be complete in 24 to 48 hours.

The proportion of hygroscopic water present in coals is very variable ; excluding the lignites, which may contain up to 30 per cent., coals, especially when freshly raised, may contain as much as 15 per cent. of water, though this limit is seldom exceeded. Broadly speaking, a good coal should not contain more than 3 to 4 per cent. of water, while in a good anthracite the percentage of water should lie between *nil* and 1·5, or at most, 2.

*Hygroscopic Water.* (*b*) *In Coke.*—According to Arth, 100 to 200 grams of coke, broken into small lumps, are weighed into a porcelain dish and dried in an air oven at 150 to 160°, until constant in weight. Samples should be kept in air-tight vessels, as they easily lose their water on exposure to air.

Hygroscopic water not only dilutes the fuel, but also reduces its calorific value owing to the heat which it

absorbs on evaporation. It is sometimes the custom to specify a certain limit for the amount of hygroscopic water in coal, and to make a proportionate deduction in the price paid if this limit is exceeded.

*Ash.*—The residue of mineral matter left on complete combustion of the coal or coke is weighed as ash. The amount of ash thus found does not represent the total amount of mineral matter originally present in the fuel, and, moreover, varies somewhat with the mode of combustion, depending, among other things, on the amount of sulphur left in the residue and the amount of carbon dioxide lost by the alkaline earth carbonates. The determination of the ash should be carried out separately, and not combined with the elementary analysis or the determination of volatile combustible matter and coke. The following directions for the determination are due to Arth :—1 to 5 grams of the finely powdered coal (or coke) are weighed off in a platinum dish or, failing this, a porcelain dish, about 7 cm. in diameter ; at first a gentle heat is applied, in order to avoid caking and subsequent difficulty in combustion, the dish being covered with a piece of platinum foil so long as there is any danger of loss by decrepitation. The subsequent heating is best carried out in a muffle furnace, the dish being placed on a piece of platinum foil, to avoid contact with the siliceous material of the furnace. The temperature is gradually raised to a bright red heat ; if the layer of ash is thick it should be cautiously stirred from time to time with a stout piece of platinum wire. When the combustion is judged to be complete, the dish and its contents are cooled in a desiccator and weighed. Complete combustion is effected with difficulty if graphitic matter is present in the residue ; unburnt carbon should be tested for in the cooled residue by adding a few drops of

alcohol, when the carbon particles will, if present, be observed floating on the liquid. In this case the alcohol should be removed by evaporation and the combustion of the residue completed over the blow-pipe flame. In difficult cases, the combustion may also be facilitated by allowing a gentle current of oxygen to impinge on the residue while it is being heated, care, of course, being taken that particles of ash are not blown away.

The proportion of ash is greatest in coals which are rich in volatile combustible matter; in these it may sometimes exceed 15 or even 20 per cent. As in the case of the water, a certain maximum limit for the ash in coal might be specified by the purchaser, say 8 or 10 per cent., and a deduction made in the price paid if the limit were exceeded. The undesirability of a large proportion of ash in coal is obvious; the ash dilutes the fuel, tends to obstruct the draught during combustion, and carries with it some of the heat of the fire, as well as unburnt fuel, on falling from the grate. Generally speaking, it may be said that a good coal should yield less than 6 per cent. of ash. The same applies to coke, especially when used for metallurgical or similar operations, in which the chemical action of the ash has to be considered.

*Volatile Combustible Matter, Combustible Residue and Coke.*—When coal is heated out of contact with air, part of the carbon is lost, mainly in the form of volatile hydrocarbons and carbon monoxide; hydrogen, oxygen, water and ammonia are given off at the same time. The non-volatile residue, which consists of an impure carbon containing the greater part of the mineral matter of the original coal, is known as coke. The total volatile matter, less the hygroscopic water, is determined as "volatile combustible matter"; the non-volatile residue, less the ash, is known as the "non-volatile combustible residue," the "fixed combustible residue," or the "fixed carbon." The latter term should be avoided, as it is somewhat misleading.

The importance of the yield and nature of the coke has already been pointed out; the yield and nature of the

volatile combustible matter are of importance if the coal is to be used for gas or tar manufacture, and the yield of volatile combustible matter, as determined by a laboratory operation, is a useful guide in classifying the coal under examination. Bearing in mind that the amount as well as the chemical composition of the volatile matter obtained from a coal vary to some extent with the conditions under which the destructive distillation is carried out, it follows, firstly, that the results of any laboratory operation should not be interpreted too literally in judging of the probable behaviour of a coal when submitted to destructive distillation on a manufacturing scale, especially as regards the nature of the distillate, and, secondly, that the estimation of the volatile and non-volatile matter should be carried out, as far as possible, under certain standard conditions in order that the results obtained may be truly comparable. The determination described should not be looked on as an exact analytical operation but as a "test" or "assay," yielding results which, if not strictly accurate, nevertheless furnish useful indications. The following method for estimating the volatile and non-volatile matter in coal is that adopted by the American Coal Committee.[1]

Place 1 gram of the undried fresh coal in a platinum crucible weighing 20 to 30 grams, and provided with a tightly fitting lid. Support the crucible on a platinum triangle, 6 to 8 cm. above the top of a Bunsen burner, which should be burning with a flame 20 cm. high when free. Heat for exactly 7 minutes in a place free from draughts. The upper surface of the crucible lid should burn clear, but the under surface should remain covered with carbon. The volatile combustible matter should be calculated on the dry coal. Duplicate analyses should agree within 0·5 per cent. The coke and non-volatile combustible residue may be estimated from the

[1] *Journ. Amer. Chem. Soc.*, Vol. XXI., pp. 1122 to 1126.

weight of the residue in the crucible, the latter by deducting the ash as previously determined.

The accompanying table shows the percentages of volatile matter yielded by the different varieties of coal, anthracite and lignite, as determined by Mahler :—

| Description of Coal. | Volatile combustible matter calculated on coal, less ash. |
| --- | --- |
| Anthracites . . . | 3 to 5 |
| Semi-anthracitic . . | 6 to 14 |
| Bituminous for steam and coking . . . | 15 to 25 |
| Bituminous for blast furnaces and forges . | 25 to 30 |
| Cannel . . . . | About 50 |
| Lignites of good quality . | About 50 |

The outstanding feature to be noticed here is the gradual diminution in the volatile matter in passing from the cannels to the anthracites. The above groups, from the cannels to the semi-anthracitic coals, inclusive, roughly correspond with the Groups 1 to 5, respectively, in the table on p. 9.

The association of a high percentage of volatile matter with a high percentage of ash is sometimes explained by the assumption that the mineral matter has enclosed the mother substance of the coal, and thus hindered its decomposition by the escape of gas.

Coke should, in view of its method of production, only contain slight quantities of volatile matter. If desired, this may be determined as described for coal.

*Sulphur.*—This constituent is usually present in coal in the form of iron pyrites and calcium sulphate. When the coal is submitted to destructive distillation part of the sulphur is driven off, chiefly in the form of organic sulphur compounds, owing to the decomposition of the pyrites. The determination of sulphur in coal and coke

is often carried out by the Eschka-Fresenius method, as follows :—

1 gram of the finely powdered material is mixed in a platinum crucible with twice its bulk of a mixture of 1 part of dry sodium carbonate and 2 parts of calcined magnesia ; the uncovered crucible is placed in an inclined position, and its lower half is heated to a low red heat till the colour of the contents changes from a grey to a yellow or brown ; it is then allowed to cool, the ash mixed with one half to 1 gram of ammonium nitrate, and heated again to redness for 5 to 10 minutes, the crucible this time being covered with a lid. After cooling, the crucible is placed in a beaker of water, and the contents detached by heating the liquid. The crucible is removed, washed carefully with water in order to remove adhering solution, and the washings added to the contents of the beaker. During the process of ignition just described, the sulphur contained in the coal or coke will have been oxidised to soluble sulphates, which may be determined in the solution by precipitating with barium chloride and weighing the precipitate, in the usual manner described in all text-books on quantitative inorganic analysis.

The limits of variation of the proportion of sulphur in coal are usually from one half to 2 per cent., while in anthracites it may only be present in the smallest traces. Generally speaking, it may be said that a good coal or coke should contain less than 1 per cent. of sulphur. It is important that coke for use in the blast furnace should contain a minimum of this constituent owing to its undesirable influence on the properties of the iron.

*Nitrogen.*—This constituent exists in the coal in the combined form, and originates from the proteins present in the original wood. When coal is submitted to destructive distillation, the nitrogen escapes mainly in the form

of ammonia, and also as aromatic amines, pyridine bases, etc. The nitrogen in coal is conveniently estimated by the method of Kjeldahl, which is very commonly used for the estimation of nitrogen in foodstuffs, fertilisers and other materials. The method depends on the destruction of the nitrogen radicles in organic compounds and their conversion into ammonium sulphate, by the action of boiling concentrated sulphuric acid in the presence of a little copper or mercury sulphate. When the digestion with the acid is complete, the mixture is made alkaline, and the ammonia distilled off into a known volume of standard acid and estimated by titration. If it is desired to include the nitrogen as nitrates and nitrites in the estimation, the method must be modified as subsequently described.

To carry out the determination, 1 gram of the powdered coal is introduced into a Kjeldahl digestion flask together with 20 c.c. of pure sulphuric acid of specific gravity 1·84, and 1 gram of granular copper oxide. The further addition of 10 grams of potassium sulphate will have the effect of shortening the process of digestion owing to the higher temperature attained through the presence of potassium bisulphate. The Kjeldahl digestion flask (see Fig. 1) should be made in Jena or other resistant glass, and should have a capacity of about 200 c.c. It is pear shaped, and has a neck about 16 cm. long and 2 cm. in diameter. Placing the charged flask in an inclined position on a piece of wire gauze, heat is carefully applied until all frothing has ceased; the mixture may then be boiled briskly until it has become perfectly clear and only retains the bright blue-green colour of the copper salt. At this stage, the flask is removed from the flame and held upright, while powdered potassium permanganate is dropped into the hot mixture in very small quantities at a time, until, after shaking, a greenish purple colour remains; in this way the complete oxida-

tion of all organic matter is ensured. After cooling water is added with extreme caution, small quantities at a time being allowed to flow down the side of the flask, while the contents are continually being agitated; the whole is transferred to a 700 c.c. flask, the total water

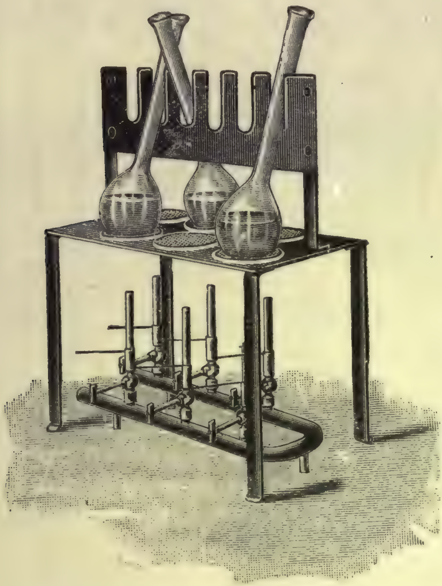

FIG. 1.—Kjeldahl Digestion Flasks on Stand.

added, including rinsings, amounting to 200 to 300 c.c. A few pieces of zinc foil are added to secure even boiling, and an excess of concentrated sodium hydroxide solution (about 100 c.c. of a saturated solution) is poured down the side of the flask in such a way as to avoid, as far as possible, its mixing with the acid liquid. Immediately after the addition of the alkali, the flask is connected up

by means of a rubber stopper to the distillation apparatus.

The accompanying illustration (Fig. 2) will give an idea as to the general arrangement of the apparatus. The

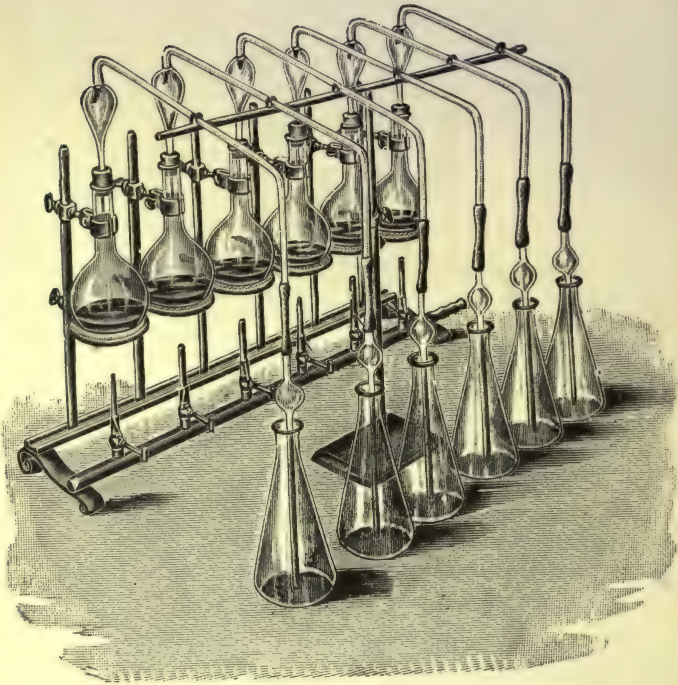

FIG. 2.—Distillation Apparatus for Kjeldahl's Process for the Determination of Nitrogen.

receiving flask contains 20 c.c. of decinormal sulphuric acid, and the tube, which dips just below the surface of the acid liquid, is provided with a bulb in order to prevent suck-back into the distillation flask. For this purpose an ordinary pipette may be used. If preferred,

the vapour may be condensed in a straight tube condenser, in which case the condenser tube should be brought near the surface of the standard acid, not dipping into the latter. If only a few analyses are to be made, ordinary Liebig condensers, fitted with adapters, may be used; if many analyses are to be made, it is more convenient to employ a series of metal tubes

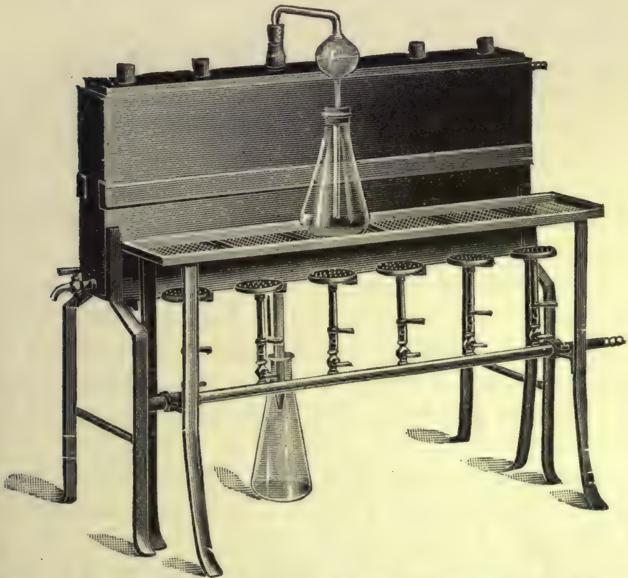

FIG. 3.—Distillation Apparatus for Kjeldahl's Process for the Determination of Nitrogen.

placed vertically in a metal tank through which water may be made to circulate, as shown in Fig. 3. Arrangements such as this, which may be obtained from most dealers in chemical apparatus, admit of a number of distillations being carried out simultaneously. What-

ever the arrangement used, the distillation flask should be connected with a bulb-trap for preventing alkaline spray from being carried over into the receiver. When the liquid has been boiled nearly to dryness, all the ammonia is certain to have been distilled over into the acid, which is then titrated with decinormal sodium hydroxide or baryta solution in order to determine the amount of ammonia absorbed. The indicator used may be litmus, methyl orange or cochineal, but not phenol phthalein.

It is generally advisable to perform the analysis in duplicate and also to do a blank test in order to determine the amount of ammonia in the materials used, which should, however, be negligible. If the analysis is carried out for the first time, a parallel determination should be carried out with a pure organic substance containing nitrogen, such as hippuric acid.

*Modification of Kjeldahl's method to include Nitrogen of Nitrates.*—It is obvious that working according to the method just described, the nitrogen of nitrates will be lost in the form of nitric acid. If it is desired to include the nitrogen present in this form, the process must be modified as follows :—

Gunning's Method: The sample is well mixed with 35 c.c. of pure sulphuric acid in which has been dissolved 3 per cent. of salicylic acid, and the whole is shaken at frequent intervals for 10 minutes. 5 grams of sodium thiosulphate and 10 grams of potassium sulphate are then added, and the mixture is carefully heated until frothing has ceased, after which it is further treated as directed above.

The above modification is especially applicable in the analysis of fertilisers, in which a considerable proportion of the nitrogen may be present in the form of nitrates.

Further instances of the application of the Kjeldahl process will be given in Chapters VI. and VII.

The proportion of nitrogen in coal may vary from 0·2 to 2 per cent. The determination of this constituent is chiefly of interest as furnishing a rough estimate of ammonia and other nitrogenous products obtainable on distillation of the coal. If this question does not come into consideration, the estimation is often omitted, and the nitrogen is grouped together with the oxygen, in the statement of the results of the analysis, both being determined by difference.

*Carbon and Hydrogen.*—The importance of knowing the percentages of carbon and hydrogen for the purpose of classifying the coal has already been pointed out in the introductory section of this chapter. The determination of the calorific value of the coal, as described below, is also based on the elementary analysis.

The method employed for the determination of carbon and hydrogen in coal is essentially the same as that employed for determining these constituents in organic compounds which contain nitrogen and sulphur. The details of the operation will be found described in many books dealing with practical organic chemistry, and will therefore not be repeated here; it will only be necessary to call attention to a few points of interest in the present case.

About half a gram of the finely powdered coal should be weighed off in a porcelain boat, about 7 cm. long and 7 to 8 mm. broad, and then mixed with about twice its bulk of dry, finely powdered copper oxide, great care being taken to avoid loss. The combustion tube should be packed throughout with lead chromate, in the usual way, in order that all sulphur may be retained as lead sulphate and prevented from escaping as sulphur dioxide, a short reduced copper spiral being placed in

the rear end, in order to decompose nitrogen oxides. While volatile matter is being distilled from the coal, oxygen should only be allowed to pass through the tube at the rate of one bubble in two seconds ; the speed may be doubled when only coke is left. The lead chromate should not be heated so strongly that it fuses with the glass of the tube ; moreover, lead sulphate, which will be formed by the interaction of the chromate and sulphur of the coal, is not quite stable at such high temperatures.

In calculating the percentage of hydrogen from the water absorbed by the drying tube, allowance must be made for the hygroscopic water, accurately determined as described above, this being deducted from the total water weighed, in order to arrive at the water formed by combustion of the hydrogen. As has already been pointed out, powdered coal is hygroscopic, so that unless the sample for analysis is preserved in a well stoppered bottle during the interval between the water determination and the elementary analysis, serious errors may be made. The re-calculation of the percentages of carbon and hydrogen on the coal, less water, ash and sulphur, has been described on p. 8. The method for calculating the calorific value of the coal from the results of the elementary analysis is described below.

*Oxygen.*—There is no direct method available for determining this constituent ; it is therefore determined by difference, deducting the sum of the percentages of the carbon, hydrogen, hygroscopic water, ash, sulphur and nitrogen from one hundred. The figure thus obtained will naturally be affected by the accumulated errors of the previous determinations ; the oxygen content is, for this and other reasons, no longer used as a basis for the classification of coals. If the nitrogen has not been estimated, both this and the oxygen will be determined together, by difference.

The amount of hydrogen found in excess of that required to combine with the oxygen in the coal (exclud-

ing, of course, the oxygen of the hygroscopic water) to form water, is known as the "disposable hydrogen." Generally speaking, the disposable hydrogen may be taken as a relative measure of the amount of gas obtainable from the coal, and an indication of the length of flame which will be produced on combustion. These relationships will be apparent on referring to the tables given above.

*Determination of the Calorific Value of Coal and Coke.*—The amount of heat theoretically obtainable from a given weight of coal or coke determines to a great extent its value as a fuel; it is often the custom to base the commercial valuation of fuels on the results of determinations of calorific value, which have been carried out on fair average samples.

The calorific value of a fuel may be stated in several ways:—

(*a*) As the number of calories produced by burning 1 kilo. of the fuel, the calorie being the amount of heat required to raise the temperature of 1 kilo. of water from 4° to 5° C.

(*b*) As the number of British Thermal Units obtainable from 1 lb. of the fuel, the B.T.U. representing the amount of heat required to raise the temperature of 1 lb. of water through 1° F. at 39·1° F.

(*c*) As the number of pounds of water which may be evaporated at the boiling point by the combustion of 1 lb. of the fuel.

*Calculation of Calorific Value from the Results of Elementary Analysis.*—This method is chosen for description in detail, as it is based on the results of processes which have already been described. The calculation is based on Dulong's assumption that the amount of heat given out on the burning of a fuel is equal to the sum of the amounts of heat produced on the combustion of its separate elements, the whole of the oxygen present being considered as already combined with sufficient of the hydrogen present in the form of water. Knowing the percentages of the carbon, disposable hydrogen and sulphur present in the coal, and the calorific values of these elements, it should be possible to calculate the

calorific value of the fuel itself. The above assumption is, of course, not theoretically justifiable, but experience has shown that when applied in the case of coal, the results obtained are sufficiently accurate for practical purposes. The present method cannot be applied to liquid fuels, as here the heats of formation of the constituent compounds are too considerable to be left out of account.

The following data are employed in the calculation :—

| | | | | | | Calories. |
|---|---|---|---|---|---|---|
| 1 kilo. | of | Carbon | in burning to | $CO_2$ | produces | 8,140 |
| 1 | ,, | Sulphur | ,, | $SO_2$ | ,, | 2,160 |
| 1 | ,, | Hydrogen | ,, | $H_2O$ as water | ,, | 34,500 |
| 1 | ,, | Hydrogen | ,, | $H_2O$ as steam | ,, | 28,900 |

In practice, it is usual to take the calorific value of hydrogen as 34,500 calories per kilo. Then if

| | | | | | |
|---|---|---|---|---|---|
| H | be the | percentage of | Hydrogen | in the | Fuel, |
| C | ,, | ,, | Carbon | ,, | ,, |
| S | ,, | ,, | Sulphur | ,, | ,, |
| and O | ,, | ,, | Oxygen | ,, | ,, |

the quantity of heat, Q calories, obtainable from 1 kilo. of the fuel is usually calculated from Dulong's formula :—

$$Q = \frac{34{,}500\,(H - \frac{1}{8}O) + 8{,}140\,C + 2{,}160\,S}{100}$$

Representative results of calorific determinations on the various kinds of coal are included in the table on p. 9. As a rule, the results obtained for coal by the method described do not differ from those obtained by the calorimetric method by more than about 3 per cent. ; in many cases the variation is less than 1 per cent. Mahler has shown that the variations in the results obtained by the two methods are considerable in the case of lignites, peat, and especially mineral oils. The calorific values of the latter fuels cannot be accurately

calculated from the carbon and hydrogen content, but must be determined by the calorimetric method, in which a known weight of the fuel is burnt in a closed bomb containing oxygen under pressure, and the heat evolved calculated from the rise in temperature indicated by a thermometer in the water contained in the calorimeter in which the bomb is placed. This method, which is often used for the determination of the calorific value of coal, is fully described in most of the works mentioned at the end of this chapter.

The heat actually available in practice naturally falls short of the amount of heat theoretically obtainable on combustion of the fuel; owing to loss of heat with the chimney gases, with the ash as it falls from the grate, radiation and incomplete combustion, the available heat is usually less than 80 per cent. of that theoretically obtainable. The results of laboratory determinations of calorific value are, however, none the less valuable, as they enable the analyst to estimate the relative heat values of different fuels or kinds of coal when used under approximately similar conditions.

### Physical Examination of Coal and Coke.

In the table on p. 9 will be found the specific gravities of the different varieties of coal; it will be noticed that there is a gradual increase in the specific gravity in passing from the varieties which contain least carbon to the anthracitic group. The determination of this constant may usually be omitted, as surer indications of the nature of the coal are obtained from a chemical examination.

It is sometimes of importance to determine the porosity and the crushing strength of coke; the latter is of importance when the coke is to be used in the blast furnace, as it should be capable of bearing the weight of the material above it without being crushed to powder, in which case it would tend to obstruct the draught. As has been pointed out previously, the nature of a coke depends, not only on the nature of the coal from which it has been prepared, but also on the method of prepara-

tion; thus, the coke produced in coking ovens is, as a rule, denser and of greater mechanical strength than that which is obtained as a by-product from gas and tar manufacture in the gas retort. The methods for determining the porosity and crushing strength of coke are fully described in Stillmann's "Engineering Chemistry."

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# CHAPTER II

## COAL TAR AND ITS DISTILLATION PRODUCTS

### INTRODUCTORY.

WHEN coal is submitted to dry distillation it yields three main products, viz., coal gas, water containing ammonia in solution, and coal tar. The present chapter deals with the examination of the latter substance and its chief distillation products, with special reference to their most important application, *i.e.*, the production of materials which form the starting points in the manufacture of dyes, disinfectants and other valuable substances, derived chiefly from the aromatic hydrocarbons. Coal tar is chiefly obtained as a by-product, either in the manufacture of coke, in which case it is known as coke-oven tar, or in the manufacture of coal gas, when it is known as gas tar. Blast furnace and generator gas tars, which are sometimes obtained as by-products in the manufacture of pig iron and producer gas, respectively, have not the same commercial importance as the two first mentioned products.

*Properties and Composition of Coal Tar.*—Crude coal tar is a dark brown or black, more or less viscous fluid, with a creosote-like smell. It is usually heavier than water, the tars having specific gravities under 1·000 being useless for the production of dyes. The latter point will be more fully dealt with below.

From what has been said in the previous chapter, it will be gathered that the proportion of tar yielded by different kinds of coal varies considerably ; the nature of the tar is influenced, not only by the quality of the coal from which it is distilled, but also to a considerable extent by the temperature at which the distillation is carried out. Generally, when low temperatures are

employed, the resulting tars consist mainly of liquid and solid paraffins, olefines and the more complex phenols. Higher temperatures, on the other hand, tend to give rise to the formation of aromatic hydrocarbons, free carbon, and phenol rather than homologues of phenol; olefines and acetylenes are formed in smaller quantities, while the paraffins practically disappear. It may also be mentioned that larger amounts of gas are formed at high than at low temperatures. These differences are explained fully in Lunge's "Coal Tar and Ammonia" (Vol. I., pp. 16 *et seq.*), where it is pointed out that the action of heat tends to encourage molecular condensations with the formation of substances such as naphthalene and anthracene, and the elimination of hydrogen, either in the elementary state, or in the form of highly hydrogenated hydrocarbons such as methane. The tendency towards the formation of phenol rather than the cresols at higher temperatures is similarly explained, while the formation of free carbon, either in a finely divided state or as a graphitic mass, may be regarded as the last stage resulting from the tendency towards molecular condensation brought into play by the action of heat.

The temperature employed in coke ovens is generally lower than in gas retorts; hence gas tar is generally richer in aromatic hydrocarbons than coke-oven tar. The majority of coke oven tars are, however, produced in such a way as to be suitable for the manufacture of dyestuffs. The most valuable tars are those from which the aromatic hydrocarbons, notably benzene, toluene and anthracene, may be conveniently isolated in a state of sufficient purity for the production of colours; for this it is essential that the tar should contain a minimum of paraffins, as these cannot conveniently be separated on a manufacturing scale, while their presence in appreciable quantities may give rise to considerable difficulty in the nitration and other chemical processes. Tars containing comparatively large amounts of open chain hydrocarbons are of no great value; they are chiefly used for the production of burning and lubricating oils and solid paraffins.

Coal tar, as produced for the manufacture of colours, contains the following substances as its most important constituents :—

Water and ammonia.

Benzene, toluene, xylenes and higher homologues of benzene.

Phenol, cresols, naphthols and other phenolic substances of higher molecular weight.

Amine bases such as aniline and its homologues.

Naphthalene, anthracene, phenanthrene and their homologues, as well as other hydrocarbons containing condensed benzene nuclei, of high molecular weight, such as pyrene and chrysene.

Pyridine, quinoline and bases of a similar nature.

Nitriles, carbazoles, etc.

Sulphur containing compounds of which the chief are carbon disulphide and thiophen.

In order to isolate the chief constituents, the coal tar is submitted to a preliminary distillation in retorts placed over an open fire. The following fractions are collected :—

(1) First runnings, up to about 120° C.
(2) Light oils or crude naphtha, up to about 170° C.
(3) Middle or carbolic oils, from 170° to 230° C.
(4) Creosote oil, from 230° to 270° C.
(5) Anthracene oil, over 270° C.

The first two fractions are often collected together, in which case they will be referred to as the " total light oils " ; they are accompanied by the aqueous ammonia which remained in the crude tar. The still residue consists of pitch.

The composition, treatment on a manufacturing scale, and especially the laboratory examination of these fractions and the products obtained from them, will be dealt with below under separate headings. The accompanying table contains figures taken from Lunge's " Technical Methods of Chemical Analysis," showing the results of the preliminary distillation of four typical tars distilled by different methods for the production of

aromatic compounds: it will be noticed that the ordinary gas tar yields more light oils and less anthracene oils than the chamber retort gas tars and the coke oven tars; further differences will be pointed out under the descriptions of the determinations of specific gravity and free carbon.

| — | Same Coal in Gas Retorts. | | Chamber Retort, Gas Tar. | Coke Oven (Otto), Tar. |
|---|---|---|---|---|
| | Vertical. | Horizontal. | | |
| Ammoniacal water . | 2·17 | 3·50 | — | 2·69 |
| Total light oil . . . | 5·85 | 3·10 | 0·40 | 1·38 |
| Middle, or carbolic oil. | 12·32 | 7·68 | 10·20 | 3·46 |
| Heavy, or creosote oil. | 11·95 | 10·15 | | 9·93 |
| Anthracene oil . . | 15·96 | 11·54 | 30·10 | 24·76 |
| Pitch . . . | 49·75 | 62·00 | 53·90 | 56·44 |
| Naphthalene . . | — | — | 4·70 | — |
| Free carbon . . | — | — | 11·10 | — |

## THE EXAMINATION OF COAL TAR.

Under this heading the determination of specific gravity and free carbon and a distillation test are described.

(*a*) *Specific Gravity*.—The water is first separated as follows: the tar is allowed to stand in a conical flask immersed in water at 50°, for 24 hours; the water collecting at the top is poured off as completely as possible, the rest being absorbed by drawing a piece of filter paper over the surface. The tar is then cooled to 15° and its specific gravity determined at this temperature. For this purpose, the pyknometer or hydrometer cannot well be used owing to the viscosity of the tar at ordinary temperatures. Lunge advises the use of an ordinary cylindrical weighing bottle of about 50 c.c. capacity, a vertical groove, about 2 mm. wide and 2 mm.

deep, being cut in the glass stopper. The bottle is weighed dry and empty, and then, when filled with water at 15°, in the usual way. It is then about two-thirds filled with the tar and placed, without the stopper, in hot water for one hour to get rid of air bubbles. After cooling, the bottle and stopper are weighed with the tar. Water is then added to fill the bottle, and the whole weighed after allowing to stand in water at 15°. From these data, the weight and volume of the tar are readily calculated, and hence the specific gravity.

As previously mentioned, the specific gravity of tars which consist mainly of aromatic hydrocarbons is usually above 1·000; if under this figure, the tar is generally not worth any further treatment. The mean specific gravity of gas tar from horizontal or sloping retorts is, according to Köhler, 1·155; from vertical retorts, according to Bueb, 1·100. Most coke-oven tars have specific gravities of the same order, *i.e.*, lying between 1·1 and 1·2. The specific gravity is influenced to some extent by the amount of free carbon in the tar.

(*b*) *Free Carbon.*—For the estimation of this constituent in tar, the following method, due to Kraemer and Spilker, may conveniently be adopted. 1 part of tar is warmed with 3 parts of aniline, and the liquid is poured on to an unglazed porous tile, which will absorb the soluble part of the tar and the aniline, leaving the insoluble carbon as a flaky mass. The latter is transferred, without loss, to a weighed watch glass, and weighed after drying in a steam oven for several hours.

As was pointed out above, the formation of free carbon is encouraged by high distillation temperatures; gas tars are therefore liable to contain more of this constituent than coke-oven tars. The carbon, which is deposited as a hard graphitic mass, remains in the retort forming part of the coke; part of the finely divided carbon, which is formed at the same time, passes over

with the tar, and part remains in the pitch after the volatile portions have been distilled off. It is possible to estimate roughly the amount of pitch which may be expected from a tar from the amount of free carbon which is contained in the latter, as good pitch of medium hardness, as produced by most tar distillers, contains, on an average, about 28 per cent. of free carbon. Tars containing a large proportion of this constituent are apt to froth on distillation.

(*c*) *Distillation Test.*—This test is carried out with a view to ascertaining the nature and approximate amounts of the various fractions obtainable on distilling the tar on a large scale; as it is hardly possible to reproduce the conditions obtaining on a manufacturing scale in an ordinary small scale laboratory operation, it is customary to distil from 3 to 5 kilos of tar in specially constructed metal vessels. Such methods will not be described here, as they cannot be conveniently carried out with the ordinary laboratory equipment; for a detailed description, including also the estimation of water in tar, see Lunge's "Technical Methods of Chemical Analysis," Vol. II., Part II., pp. 761 *et seq.*

The following small scale operation, devised by B. Nickels, is described, as it will afford an opportunity of studying the behaviour of coal tar on distillation, and provide further material for analytical work: 250 c.c. of tar are introduced into a glass retort of 750 c.c. capacity; the retort is placed on a cup-shaped piece of coarse wire gauze which rests in a circular hole in a piece of sheet iron. No thermometer or special condensing apparatus are necessary, and the heat is supplied by means of a powerful Bunsen burner which is protected from draughts by asbestos screens. The retort is covered by a dome, which may be made from a tin can, a trifle larger than the bulb of the retort, by cutting out a piece from its side in order to make room for the neck. The heating is regulated so that the distillate falls in

drops in rapid succession; towards the end, it will be necessary to heat strongly, so that the wire gauze becomes red hot; when the pitch begins to intumesce, the heating is discontinued. If the distillate solidifies in the tubulure, it is melted down by cautiously heating with a Bunsen flame. The distillate is divided into the following fractions:—

(1) Ammoniacal liquor and total light oils.
(2) Middle and heavy oils.
(3) Anthracene oils.

Fraction (1) is collected in a graduated cylinder, which is changed for a small weighed beaker as soon as a drop of the distillate solidifies when dropped into water. The amount of total light oils will be too small for examination; after reading off their volume, they are separated from the ammoniacal liquor, which may then be titrated by means of standard acid, in order to estimate the ammonia. The second fraction will, at first, consist largely of solid naphthalene, and will afterwards become more liquid. When a drop of the distillate, collected on a cold metal surface, deposits yellow or greenish amorphous matter, the receiver is changed for a second small weighed beaker in which the last fraction is collected until the heating is discontinued. The second and third fractions may be weighed, the former being assayed for phenols, or tar acids, and the latter for anthracene, by methods subsequently described. When the retort is nearly cold it is plunged into cold water; the pitch will then shrink, so that it may be removed in a lump on breaking the retort, and weighed. Knowing the volume of the tar distilled and its specific gravity, the percentage amounts of the various constituents weighed may readily be calculated.

During the first stages of the distillation, the presence of water may cause bumping; should the inconvenience caused thereby be serious the tar should first be freed from water by the method described under the determination of the specific gravity.

The above process must, of course, not be regarded as an exact analytical operation; apart from the fact that unavoidable losses of the lighter constituents will occur, it must be borne in mind that the relative amounts of the various fractions may vary according to the rate of the distillation. Operations of this nature should always be carried out under exactly similar conditions, if comparable results are desired.

## The Examination of First Runnings and Light Oils.

When these two fractions are collected together, as is often the case, they are known as "first light oils," "crude or once run naphtha," or "total light oils." For the sake of clearness, the latter term will be employed to signify the total distillate, exclusive of ammoniacal liquor, resulting from the first distillation of coal tar, up to the point at which the distillate becomes heavier than water. The products coming under this heading are usually yellow to dark brown, mobile liquids of a penetrating smell recalling ammonium sulphide, carbolic acid and naphthalene, at the same time. A green fluorescence is sometimes observable, owing to tar carried over in small quantities during the distillation. The total light oils are usually completely volatile below 180° on redistillation, and have specific gravities ranging from 0·910 to 0·950.

According to Kraemer and Spilker (Muspratt-Bunte's "Chemistry," Vol. VIII., p. 16), the composition of the total light oils is as follows:—

Phenols, consisting of phenol, cresols (chiefly meta cresol) and small quantities of xylenols, 5 to 15 per cent.

Bases, chiefly pyridine and its homologues, 1 to 3 per cent.

Sulphur compounds, consisting of carbon disulphide, thiophen and its homologues, 0·1 per cent.

Nitriles, such as aceto and benzo-nitriles, 0·2 to 0·3 per cent.

Neutral oxygen compounds, such as acetone and coumarone, 1·0 to 1·5 per cent.

Hydrocarbons, 3 to 5 per cent. being olefines from hexylene and upwards, 0·5 to 1·0 per cent., paraffins beginning from hexane, and 1·0 to 1·5 per cent., unsaturated compounds which combine with bromine at the ordinary temperature, such as cyclopentiadenes and the hydrobenzenes.

The remaining 80 per cent. consists of aromatic hydrocarbons, of which about four-fifths belong to the benzene series, and one-fifth to the naphthalene and other series, including hydrocarbons of higher molecular weight. The benzene hydrocarbons consist approximately of benzene, 100 parts ; toluene, 30 parts ; xylenes, 15 parts ; trimethyl benzenes, 10 parts ; tetramethyl benzenes, 1 part ; together with traces of higher methylated and ethylated benzenes.

Although, as will be gathered from the above list, the light oils are exceedingly complex mixtures, the tests to which they are usually submitted in the laboratory are limited to (*a*) the determination of specific gravity, (*b*) fractional distillation, and (*c*) the estimation of phenols. These tests will, at any rate, enable the analyst to distinguish between first runnings, light oils and total light oils ; in order to fully understand the significance of the results obtained, it will, however, be necessary to have considerable experience in dealing with the products in question, both in the laboratory and on a manufacturing scale. Further chemical tests are applied to the purer products obtained from the first runnings and light oils on distillation. (See below, under "Benzols, Commercial Benzene, Toluene and Xylene.")

(*a*) *Specific Gravity.*—This may be determined by means of an ordinary hydrometer or specific gravity

float, or more accurately, by means of a Westphal or Mohr balance. An instrument of this type is shown in Fig. 4. For use, it is mounted as shown, the thermometer plummet being suspended in distilled water at 15° from the end of the graduated beam by means of a fine platinum wire; equilibrium is established by means of the adjusting screw, with weights corresponding to a specific gravity of 1·0000 on the beam. Each of the largest weights corresponds to 0·1 in the figure for the specific gravity; one of these may therefore be suspended from division 10, or two of them from division 5 when making this preliminary adjustment. The vessel containing the water is then removed, and the plummet is wiped dry and suspended in the liquid of which the specific gravity is to be determined, without disturbing the adjustment of the instrument. The temperature of the liquid should be the same as that of the water which it has replaced. The pointer of the balance is then brought back into its original position by adjusting the necessary weights on the graduated arm; as each weight weighs ten times as much as the next smaller size, the specific gravity may be directly read off without any calculation. If the specific gravity float is used, it will also be necessary to have the liquid at 15°.

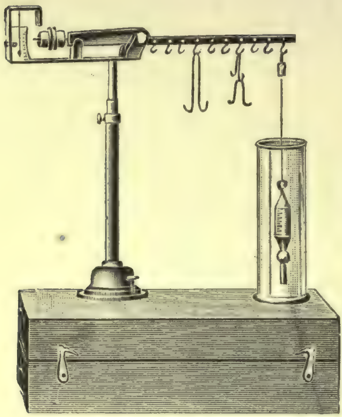
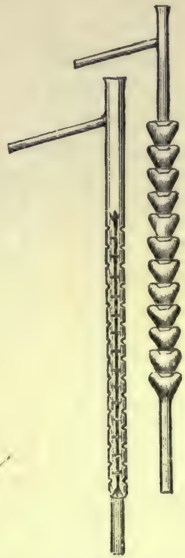


FIG. 4.—Westphal Specific Gravity Balance.

The specific gravity of the total light oils usually lies between 0·910 and 0·950. The average specific gravity of English first runnings is 0·900, and that of light oils 0·975. The indications furnished by this test are not so definite as those obtained from the two following tests.

(*b*) *Distillation Test.*—For the carrying out of this test, several methods are in use, and it is, therefore, necessary to exercise some caution in comparing results obtained by different analysts. The most reliable and scientifically accurate method is that generally employed in Germany, which consists in distilling the liquid from a flask fitted with an effective fractionating column. When such an appliance is inserted between the distillation flask and the condenser, the higher boiling portions of the liquid which might otherwise be carried over with the vapours, are condensed and run back into the flask; a more complete separation of the constituents according to their boiling points is thus obtained. For the present purpose, Lunge recommends the use of a three bulb Linnemann apparatus or the Hempel tube. Sidney Young's "Pear" and "Rod and Disc" forms, figured here, are also very efficient for the fractionation of benzols.



FIGS. 5 and 6.—Sidney Young's "Rod and Disc" and "Pear" Fractionating Columns.

The thermometer should be placed so that the upper end of the bulb is on a level with the bottom of the

side tube of the column. A straight tube Liebig condenser is used, and the distillate is received in graduated cylinders. 300 c.c. of the liquid may be distilled from a 500 c.c. flask, and the volume of the distillate noted every 10°, from 80° and onwards.

From the results thus obtained, an approximate idea may be formed as to the composition of the liquid, which will give some indication of the portions of the coal tar distillate of which it is composed. Working with larger quantities, preferably freed from carbon disulphide, as described below, benzene, b.p. 80° to 81°, and toluene, b.p. 110° to 111°, may be separated in a state of purity. Ortho, meta and para-xylenes, boiling at 142°, 139° and 138° respectively, are obtained as a mixture; they cannot be separated by fractional distillation.

Good first runnings should, according to Lunge, yield at least 10 per cent. by volume, below 100°, and when the product collected up to 130° is redistilled, it should yield at least 25 per cent. of its volume below 100°. First runnings yield, on an average, about 78 per cent., by volume, below 171°.

Light oils should yield little below 120°, and about 30 per cent. by volume, between 120° and 171°. All which comes over above the latter temperature belongs, properly, to the carbolic oil fraction. If an appreciable amount distils below 120°, the oil probably contains first runnings, while if the total yield up to 171° falls considerably below 30 per cent., a portion of the coal tar distillate, properly belonging to the carbolic oil, has probably been allowed to run into the light oil.

(*c*) *Determination of Phenols.*—The following rapid method does not yield results of great accuracy, but may conveniently be adopted in technical work. It is based on the solubility of the phenols, and the insolubility of the neutral oils in caustic alkali solution. 50 c.c. of the sample are introduced into a graduated glass-stoppered

cylinder of about 250 c.c. capacity, and 100 c.c. of a 9 per cent. solution of sodium hydroxide are gradually added. The whole is well mixed by shaking, and allowed to stand until it has separated into two well defined layers; the volume of the neutral oils is then read off and subtracted from the original volume of the sample; the difference is taken as an approximate measure of the phenols present. A more accurate reading is got by adding a volume of petroleum either equal to that of the sample, deducting this from the final reading.

More accurate methods for estimating phenols are given below, when dealing with the purer products.

| | Percentage Distilling below | | | | Sp. Gr. at 15·5° C. | Approximate Composition. |
|---|---|---|---|---|---|---|
| — | 100° C. | 120° C. | 130° C. | 160° C. | | |
| 90 per cent. benzol. | 90 | — | — | — | 0·880 to 0·888 | 70 per cent. benzene, 24 per cent. toluene, traces of xylene, 4—6 per cent. carbon disulphide and light paraffins, etc. |
| 50 per cent. benzol. | 50 | 90 | — | — | 0·880 to 0·872 | Chiefly toluene and xylene with a little benzene. |
| 30 per cent. benzol. | 30 | 90 | — | — | 0·875 | Chiefly toluene and xylene. |
| Solvent naphtha | *Nil* | — | 8—30 | 90 | 0·875 | Chiefly xylene and higher homologues with a little naphthalene and paraffins, etc. |
| Burning naphtha. | *Nil* | — | — | 30 | 0·885 | Chiefly xylene and higher homologues; naphthalene and paraffins, etc. |

Light oil is used as such, for making varnishes for wood and iron, and occasionally also as an illuminant and as a solvent for pitch. By far the most important use of light oil, as well as first runnings, is in the manufacture of the "benzols" of commerce, from which benzene, toluene and xylene may be produced in a state of purity for the manufacture of colours and other valuable products.

Before redistillation, the first runnings or light oil is washed, first with dilute sulphuric acid to remove pyridine bases, then with concentrated sulphuric acid to remove olefines and other unsaturated compounds such as coumarone, indene, cyclopentadiene, etc., which are converted into resins, and finally with dilute alkali to remove phenols.

The chief products resulting from the distillation of the washed light oils of tar are set out in the table on p. 45, together with their behaviour on further fractionation, specific gravities and approximate compositions. The results quoted here have been collected from data given by Lunge and Allen.

## The Examination of Benzols and Commercial Benzene, Toluene and Xylene.

The tests commonly applied to these products, some of which are described in the accompanying table, are (*a*) the determination of specific gravity; (*b*) the investigation of behaviour on fractional distillation; (*c*) the estimation of carbon disulphide; and (*d*) the estimation of non-nitratable hydrocarbons. Carbon disulphide occurs chiefly in 90 per cent. benzols (see table), and only in comparatively small amounts in the higher boiling benzols; its presence in appreciable quantities, in benzene which is to be nitrated, is objectionable. Light hydrocarbons, including olefines, consisting mainly of pentene, and paraffins, occur chiefly in the low-boiling benzols, though higher open chain hydrocarbons are often met with in the heavy benzols and in commercial toluene and xylene. The presence of such impurities in appreciable amounts is highly

objectionable, causing trouble in the nitration process, and lowering the yield of amines. Commercial benzols are sometimes adulterated with petroleum spirit, which consists chiefly of heptane, or with shale naphtha, which contains about 50 per cent. of olefines, mainly heptene, and about 50 per cent. of paraffins.

In addition to the above-mentioned tests, the following tests for determining the relative purity of benzene, toluene and xylene are described: (*e*) the bromine absorption test, and (*f*) the sulphuric acid test. Under the heading Xylene will be described the estimation of of meta-xylene in presence of its isomers.

The value of a benzol depends, firstly, on its relative freedom from the undesirable impurities mentioned above, and secondly, on the proportion of benzene or toluene present, the latter substances being two of the most valuable constituents of coal tar. As regards the xylenes, only the meta isomer is of any value to the colour manufacturer, the ortho and para isomers being looked on as undesirable impurities.

(*a*) *Specific Gravity.*—This is best determined by means of the Westphal balance, as described on p. 42.

The indications afforded by this test are not always of a very definite nature. In the case of 90 per cent. benzol, a high specific gravity may generally be taken as pointing to the presence of an appreciable quantity of carbon disulphide. The specific gravity of coal tar naphtha should never be below 0·870; if lower, light paraffins are probably present, as the specific gravity of petroleum spirit is, at the most, only very little over 0·700. On the other hand, the effect of the presence of carbon disulphide on the specific gravity counteracts that of the light paraffins, so that a sample containing both of these impurities may well have a normal specific gravity.

(*b*) *Fractional Distillation.*—This may be carried out as described under the heading of Light Oils and First Runnings; the volume of the distillate should be noted at

the temperatures given in the last table, for comparison of results.

The products dealt with under the present heading distil within narrower limits of temperature than the crude coal tar distillates from which they are derived, the constancy of boiling point of a sample naturally depending on the number of times which it has been redistilled with a view to purification. The terms "90 per cent. benzol," "50 per cent. benzol," etc., refer to the proportion of the original sample which distils below and up to 100°. According to Allen, a good 90 per cent. benzol should not distil below 80°, and only yield 20 to 30 per cent. below 85°, and not more than 90 per cent. below 100°. It should be wholly distillable below 120°. If, say, 35 to 40 per cent. distils below 85°, too much carbon disulphide or light hydrocarbons are probably present.

50 per cent. benzol should distil wholly below 130°, and should yield 50 per cent. below 100° and 40 per cent. between 100° and 120°.

30 per cent. benzol should yield 30 per cent. below 100° and 60 per cent. from 100° to 120°

Pure benzene, toluene and xylene of commerce distil within 1° C.

For the quantitive estimation of the pure benzenoid hydrocarbons on a large scale, see Lunge's "Coal Tar and Ammonia," Vol. II., pp. 774 *et seq*.

(*c*) *Carbon Disulphide.*—The process for the estimation of this constituent, now to be described, depends on the formation of potassium xanthate by the interaction of carbon disulphide and potassium ethoxide as follows:—

$$\begin{matrix} C_2H_5 \\ K \end{matrix}\Big\rangle O + CS_2 = S < C\Big\langle\begin{matrix} OC_2H_5 \\ SK \end{matrix}$$

The precipitated xanthate is separated and estimated by titration with standard copper sulphate solution, or analysed for sulphur.

If the sample should be turbid owing to the presence

of water, it should first be dehydrated by shaking up with plaster of Paris and filtering. For the estimation, Kraemer and Spilker recommend the following process: 50 grams of benzol are mixed with 50 grams of alcoholic potash, made by dissolving 11 grams of potassium hydroxide in 90 grams of absolute alcohol; the whole is then shaken at intervals during several hours. If carbon disulphide is present, the xanthate will separate out in yellow silky needles. The latter are separated in aqueous solution by shaking the mixture with 100 c.c. of water in a separating funnel and washing the remaining benzol with successive small quantities of water which are added to the main aqueous extract.

The xanthate may then be estimated in the aqueous solution as follows: A solution containing 12·475 grams of crystallised copper sulphate per litre is prepared; 1 c.c. of this corresponds to 0·0076 gram of carbon disulphide in the titration described below. The aqueous xanthate solution is acidified with dilute acetic acid, whereupon it must immediately be titrated with the copper solution, as free xanthic acid decomposes spontaneously. A brown precipitate of cuprous xanthate will be formed at first; on the addition of more of the copper solution, this precipitate is transformed into the bright yellow cupric xanthate. The end point is reached when a drop of the solution taken out on a glass rod, and placed beside a drop of dilute potassium ferrocyanide solution on a piece of filter paper, produces a red mark at the point of contact of the liquids; the amount of copper solution which has been added should then be in slight excess of that required to interact with the whole of the xanthic acid present, to form the insoluble cupric xanthate. The amount of carbon disulphide in the sample may then be calculated from the number of c.c.

of copper solution used, by employing the factor given above.

The following alternative methods may also be employed :—

(i.) The acidified solution of potassium xanthate is treated with an excess of copper sulphate solution, and the precipitated cupric xanthate filtered off, washed, ignited and determined as cupric oxide or copper, as usual.

(ii.) The potassium xanthate solution is warmed with an excess of potassium hydroxide solution and bromine till perfectly clear ; the sulphur, which will now all be present as alkali sulphate, is determined by precipitation with barium chloride in presence of hydrochloric acid in the usual way.

After the removal of the carbon disulphide, the residual benzol should be examined by distillation and tested for its specific gravity ; a reduction both in the amount of distillate coming over below 85° and in the specific gravity should be noticeable if the sample contained an appreciable amount of the impurity.

The quantity of alcoholic potash recommended above is sufficient for the removal of quantities up to 5 per cent. of carbon disulphide. In very exceptional cases only will the percentage of carbon disulphide in 90 per cent. benzol exceed this limit ; usually it only amounts to 1 to 2 per cent. In 50 per cent. benzol it may sometimes amount to as much as 1 per cent., while in the higher boiling products, it is either entirely absent or present in traces. The pure benzene of commerce may contain from about 0·1 to 0·3 per cent. of carbon disulphide. As was mentioned above, benzene or toluene which is to be nitrated should be as free as possible from this impurity.

(*d*) *Non-Nitratable Hydrocarbons.* — The so-called "nitrofication test," for the estimation of benzene, and non-nitratable hydrocarbons, by nitrating the benzol,

will not be described here, owing to its inaccuracy. The following method, due to Frank, Kraemer and Spilker, is based on the fact that the benzenoid hydrocarbons are converted, at the ordinary temperature, into water-soluble sulphonic acids ; the oily residue which is unacted on by the acid may consist of paraffins, naphthenes (*i.e.*, hydrogenated aromatic hydrocarbons) and carbon disulphide.

200 grams of the sample are placed in a separating funnel, and 500 grams of fuming sulphuric acid, containing 20 per cent. of the anhydride, are cautiously added in small amounts, shaking well after each addition. When the whole of the acid has been added, the mixture is shaken for 15 minutes, and then allowed to stand for 2 hours to separate. The lower acid layer is run off, and the upper layer is treated with two successive portions of 500 grams of the fuming acid as just described. The oily layer is separated off, and the acid extracts are united and run slowly and cautiously on to an equal weight of pounded ice. Care should be taken that the temperature does not rise above 40°. The diluted acid will contain a certain quantity of oily residue, unacted on by the fuming acid, which has either been dissolved by the sulphonic acids, or mechanically removed from the main portion. This is separated by distilling the mixture from a flask, over a free flame, the distillate being caught in a small separating funnel. When, apart from any oil which passes over, 50 c.c. of liquid have been collected, the distillation is discontinued, and the oily portion of the distillate separated from the aqueous layer and added to the main portion of the oily matter which was unacted on by the fuming acid. The latter is treated with successive portions of 30 c.c. of fuming sulphuric acid as described above, until no further sensible diminution in volume takes place. The residual

oil is washed with a small quantity of distilled water in the funnel, separated carefully, transferred to a tared flask and weighed. If the carbon disulphide has previously been determined, it may be deducted from the total non-nitratable matter. The remainder will consist of paraffins, and possibly also of naphthenes.

By this method, the presence of an undesirable amount of paraffins, which in some cases may be due to adulteration with petroleum spirit or shale oil, may be detected. Benzols should only contain a few tenths per cent. of paraffins, or at the most, only 1 per cent. Commercial xylenes, however, sometimes contain up to 3 per cent. of this impurity.

The following tests are sometimes applied in order to determine the relative purity of commercial benzene and toluene or benzols :—

(*e*) *Bromine Absorption Test.*—This test, devised by Frank, Kraemer and Spilker, gives an indication of the amount of hydrocarbons present, which combine with bromine at the ordinary temperature, *i.e.*, unsaturated compounds, which should have been removed during the treatment of the benzol with strong sulphuric acid. (See p. 46.) It is not applicable to xylene or to mixtures containing much of this constituent.

A tenth normal bromine solution is prepared by dissolving 9·9167 grams of potassium bromide and 2·7833 grams of potassium bromate in water and making up to 1 litre ; 1 c.c. of this solution will liberate 0·008 gram of bromine on acidification with dilute sulphuric acid.[1]

5 c.c. of the sample are placed in a stoppered bottle of about 50 c.c. capacity, together with 10 c.c. of 20 per cent. sulphuric acid, and as much of the bromide and bromate solution as the sample will decolorise after shaking uninterruptedly for 5 minutes is quickly added.

[1] $5\,KBr + KBrO_3 + 6\,H_2SO_4 = 6\,KHSO_4 + 3\,H_2O + 3\,Br_2$.

The end point is indicated when the oil floating on the top shows an orange red after standing for 15 minutes, and a drop of it momentarily produces a dark blue colour on zinc iodide and starch paper. Preliminary trials must be made in order to determine how much of the bromine solution will be required, for in the actual determination it is necessary that the full amount should be added at once, as directed above.

Pure benzene or toluene of commerce should give a distinct permanent colour after adding only 0·1 c.c. of the bromine solution. Commercial 50 per cent. or 90 per cent. benzols require, on an average, 0·6 c.c. and rarely more than 1 c.c.

(*f*) *Sulphuric Acid Test.*—This test is also due to Frank, Kraemer and Spilker; it gives an indication of the relative amount of matter present which will react with strong sulphuric acid at the ordinary temperature. (Compare introductory remarks to the bromine absorption test.)

5 c.c. of the sample are vigorously shaken with 5 c.c. of concentrated sulphuric acid in a stoppered bottle, for 5 minutes, and then compared with a solution of potassium dichromate in 50 per cent. sulphuric acid, contained in a similar bottle. 50 and 90 per cent. benzols should exhibit a colour like that of a solution containing 0·5 to at most, 1·5 gram of chemically pure potassium dichromate per litre. Xylene will give a colour like a solution containing 1·2 to 2·0 grams per litre, while pure benzene or toluene of commerce should give no colour at all.

## XYLENE.

The xylene as obtained by the distillation of coal tar contains the three isomeric dimethyl benzenes in varying

proportions, together with smaller quantities of the higher benzene homologues and paraffins. Of these constituents, meta xylene is the only one of any use in the manufacture of dyestuffs; the ortho and para isomers are not only useless for this purpose, but have to be removed before the chemical treatment of the meta xylene is proceeded with. Paraffins are a very undesirable impurity and may render the xylene unfit for colour making, if present in large amounts. The following variations in composition of xylenes from English and Scotch tars were found by Levinstein:—Paraffins, 3 to 10 per cent., ortho xylene, 3 to 15 per cent., para xylene, 3 to 10 per cent., and meta xylene, 70 to 87 per cent.

In practice, most of the ortho xylene is usually removed as sulphonic acid in the treatment of the benzol with sulphuric acid (see p. 46); meta xylene may be separated from its isomers by converting the mixed xylenes into sulphonic acids and then steam distilling, when only the meta xylene will be regenerated.

*Determination of Meta Xylene and Paraffins in Crude Xylene.*—The method described here is due to Crafts. A weighed quantity of xylene, about 10 to 20 grams, is poured on to two and a half times its weight of concentrated sulphuric acid contained in a tube of hard glass; the depth of the xylene layer in millimetres is noted, after which the tube is sealed and heated to 120° for 1 hour, the contents being well mixed by shaking from time to time. After cooling, the tube is opened, and the contents are treated with 3 to 4 times their bulk of a mixture of equal parts of concentrated hydrochloric acid and water, shaken well and allowed to stand for 1 hour at the ordinary temperature. The insoluble oily layer, which consists of saturated hydrocarbons, chiefly paraffins, is measured in the tube by noting its depth in millimetres, or better still, separated off in a funnel, distilled and weighed. The solvent acid is returned to

the tube, which is then resealed and heated to 122° for 20 hours. After this treatment, an oily layer will have been formed which will consist of approximately 97 per cent. of the meta xylene; this may be measured, or separated, distilled and weighed; of the xylene sulphonic acids formed during the heating with sulphuric acid, only that derived from the meta xylene is decomposed by heating with hydrochloric acid under the conditions of the experiment. For the estimation of ortho and para xylenes and ethyl benzene by a continuation of this process, see Crafts, *Comptes Rendus*, 114, p. 1110.

### Distinction between Coal Tar Benzol, Petroleum Spirit and Shale Naphtha.

These products, though similar as regards appearance and boiling points, may be distinguished by their smell and specific gravities. Thus the specific gravity at 15° of benzols is practically always above 0·85, while the specific gravities of petroleum spirit and shale oil are considerably lower, usually about 0·700 and 0·72, at 15° respectively. The chemical distinction already alluded to is based on the fact that the paraffins are unacted on by fuming sulphuric acid at the ordinary temperature, while the aromatic hydrocarbons are converted into sulphonic acids. The resistance of the former to the nitrating action of a mixture of nitric and sulphuric acids may also be mentioned here. Petroleum spirit contains over 75 per cent. of paraffins, the rest being mainly olefines; shale naphtha consists of approximately equal parts of paraffins and olefines. The latter are, as is well known, absorbed by strong sulphuric acid, usually with some darkening in colour.

The following simple tests may be used for the

differentiation of benzol on the one hand and petroleum spirit and shale naphtha on the other: (i.) Coal tar pitch dissolves freely in the former, but only slightly in the latter, producing a comparatively feeble colouration; the distinction may be made still sharper by using pitch which has previously been exhausted with petroleum spirit. (ii.) Picric acid dissolves in the aromatic hydrocarbons giving a yellow solution, but is insoluble in the two other products under consideration. (See also Chapter V., p. 163.)

## The Examination of Middle or Carbolic Oil and its Products.

The principal constituents of this fraction are phenols and naphthalene, of which phenol itself, *i.e.*, monohydroxy benzene, is the most valuable. At the ordinary temperature a large portion of the naphthalene crystallises out from the oil; at 40°, middle oil is a brownish yellow liquid, smelling of carbolic acid and naphthalene. Its specific gravity at 15°, which may be determined as described for crude coal tar, generally lies between 1·00 and 1·03; if under the lower limit an unduly large amount of light oils may be present. The crude naphthalene present amounts to 30 per cent. or more. In practice the greater part of the naphthalene is separated by filtration. The remaining carbolic oil, which contains phenol, cresols, xylenols and other higher phenols, neutral tar oils, water, naphthalene, pyridine bases, etc., is either sold as such for disinfecting purposes or varnish making, or it is treated with caustic alkali solution in order to separate the phenols from the neutral and basic constituents. The phenols are recovered from the alkaline solution by precipitation with mineral acid, and worked up for carbolic or cresylic acids of varying degrees of purity, by fractional distillation and other processes; the portion insoluble in alkali is worked up for heavy solvent naphtha, pyridine bases, and naphthalene.

*Crude Naphthalene in Middle Oil.*—500 grams of the middle oil are cooled and the naphthalene is separated by filtration, pressed between filter paper until no longer oily, and weighed. It should distil mainly between 210° and 220°.

## Crude Carbolic Acid.

This includes the portion of the middle oil which is liquid at the ordinary or lower temperatures, having been separated from the solid crude naphthalene by filtration. According to Lunge, it should have an average boiling point of 250°, a specific gravity between 0·99 and 1·01, and contain from 25 to 35 per cent. of phenols and about 5 per cent. of pyridine bases. It may be examined for (*a*) total phenols and water, and (*b*) phenol, *i.e.*, the monohydroxy benzene.

(*a*) *Total Phenols and Water.*—The following approximate method is due to Bach; advantage is taken of the insolubility of the phenols in brine, and their solubility in sodium hydroxide solution.

50 c.c. of the sample are distilled from a retort until solid matter begins to come over, the distillate being caught in a clean wide 100 c.c. burette, graduated in fifths of a c.c. and furnished with a glass tap. Before the distillation 25 c.c. of a saturated solution of common salt are introduced into the burette, and the level of the liquid is noted. If the carbolic acid contains no water the oil separates clearly from the brine, while if the contrary is the case, an emulsion is formed which may, however, be broken down by gently agitating the liquid and allowing to stand. When the layers have become distinct, the level of the brine is read off; its increase in volume is a measure of the water in the sample. The brine is then drawn off, the level of the oil noted and the burette filled to the zero mark with sodium hydroxide

solution of specific gravity 1·26; after closing with a cork the contents are mixed by shaking vigorously and then allowed to settle. If the burette was originally clean and free from grease the oil will have separated after half an hour, when its level may be observed. The difference between this and the previously observed volume of the oil gives the amount of phenols in the sample.

The percentage of phenols in crude carbolic acid is very variable, especially as the inferior qualities are often adulterated with neutral tar oils. The percentage of phenols is usually stated in naming the product, *e.g.*, "carbolic acid, 25 per cent.," "carbolic acid, 50 per cent."

There is no satisfactory method of determining the naphthalene or the relative proportions of phenol, cresols and higher phenols in crude carbolic acid, though the following process, due to Chas. Lowe, will furnish results which will give a rough idea of the proportion of phenol present in a sample which has not been adulterated with neutral oils.

(*b*) *Phenol.*—This method combines separation by distillation with the determination of solidifying point of the distillate. Comparison is made with the solidifying points of mixtures containing known proportions of pure phenol and cresols; for this purpose Calvert's pure products may be used.

100 c.c. of the sample are distilled from a retort, and the distillate is collected in graduated tubes. At first water distils and then an oily fluid; when 10 c.c. of the latter have been collected, the receiver is changed. The volume of the water is read off; if the oily liquid floats on the water, it is light oil of tar; if it sinks it may be regarded as hydrated phenol, containing about 50 per cent. of phenol. The next portion which distils consists

of anhydrous phenols; when it measures 62·5 per cent., the receiver is again changed. The residue is wholly cresols and higher phenols. The fraction consisting of 62·5 per cent. is cooled and its solidifying point determined; this should lie between 15·5° and 24°. The proportion of phenol to cresols in the fraction may then be estimated by determining the solidifying points of synthetic mixtures of pure phenol and coal tar cresol.

| — | Crude Carbolic Acid from Tar from | | |
|---|---|---|---|
| | Blackburn. | Manchester. | Manchester. |
| Water, per cent., by volume | 12 | 13 | 15 |
| First oil up to 185 (to be rejected) per cent. . | 11 | 11 | 10 |
| Carbolic acid distilling below 190° per cent. . | 48 | 45 | 45 |
| Ditto above 190° . . | 13½ | 17½ | 17½ |
| Solidifying points of the latter, *i.e.*, 61 to 62 per cent. of the total sample. | 15° | 18° | 16¾° |

The solidifying point may be determined as described under "Crystallised Carbolic Acid." (See p. 63.)

The proportion of light oils in crude carbolic acid is usually small, at the most 5 to 6 per cent., hence an appreciable quantity of phenol may be lost in the first 10 per cent. of oily matter distilled. In some cases, therefore, it may be best to take the solidifying point of the distillate coming over between 185 and 195°. When dealing with better qualities, *i.e.*, those containing more phenol, it is recommended to take the solidifying point

of the distillate coming over between 180 and 190°, as in such cases the whole of the phenol will naturally come over at lower temperatures. The temperatures referred to are indicated by a thermometer, the bulb of which is placed in the vapour of the boiling liquid.

The table on p. 59 contains results obtained by Watson Smith by the method just described.

The neutral oils may amount to as much as 10 per cent., and the water may lie between 10 and 17 per cent. If an excess of cresylic acid is present, crystallisation is prevented in the determination of the solidifying point; in this case, a second fractional distillation should be made, this time stopping when the thermometer, placed in the vapour, indicates 190°.

The melting and boiling points of phenol and the three cresols are as follows:—

| — | Phenol. | Ortho Cresol. | Meta Cresol. | Para Cresol. |
|---|---|---|---|---|
| Melting points ° C. . | 42·5—43 | 30—31 | 4 | 36·5 |
| Boiling points ° C . | 182 | 190·5 | 200—201 | 201·8 |

The relative proportions of the three cresols in coal tar are about 35 per cent. ortho, 40 per cent. meta and 25 per cent. para. The mixture of cresols from coal tar boils from 198° to 203°.

### Pure Carbolic Acid and its Preparations.

The crystallised pure carbolic acids of commerce consist of more or less pure phenol; they may contain small quantities of cresols and higher boiling compounds which produce a red or yellow colour, water and traces of metallic compounds.

Liquefied pure carbolic acid usually consists of about 90 parts of pure phenol and 10 parts of water or alcohol. It may be distinguished from "liquid carbolic acid,"

which usually consists of cresols and higher homologues by the two following tests (*a*) and (*b*) :—

(*a*) *Boiling point.*—Liquefied pure carbolic acid begins to boil below or near 100°, after which the boiling point quickly rises to 185° to 190°, while the product containing cresols will boil at 185° to 209°.

(*b*) *Solubility in water.*—The liquefied product requires at most 18 parts of water to give a clear solution, while cresylic acid is not completely dissolved by even 50 parts of water.

*Estimation of Phenol.*—The method to be described is Koppeschaar's modification of Landolt's process, based on the formation of the insoluble tribromophenol by the interaction of phenol and bromine in aqueous solution. A known amount of bromine having been added to the phenol solution, potassium iodide solution is added, whereupon an amount of iodine corresponding to the excess of free bromine present is liberated; this is estimated by titration with standard sodium thiosulphate solution, using starch as indicator. The amount of bromine used up in the formation of tribromophenol may then be calculated. It should be noted that this method is only applicable to the products dealt with under the present heading, *i.e.*, pure or nearly pure phenol, or solutions of the latter which do not contain cresols or other substances which also react with bromine water. The following solutions will be required :—

*A solution of sodium thiosulphate*, corresponding to 5 grams of iodine per litre (5 grams I = 9·764 grams $Na_2S_2O_3$ 5 $H_2O$). This solution may be standardised according to Volhardt's method, as described on p. 92.

*Potassium iodide solution.*—A 10 per cent. solution of the pure salt in water.

*Starch solution.*—Freshly prepared by heating half

a gram of powdered starch with 50 c.c. of water in boiling water.

*Bromine solution.*—A solution containing 5 molecular proportions of potassium bromide to one of potassium bromate, of such a strength that 50 c.c. mixed with 5 c.c. of strong hydrochloric acid and 100 c.c. of water[1] requires for complete decolorisation 86 to 95 c.c. of the thiosulphate solution described above. It may be prepared either by dissolving the pure salts in water, in the requisite proportions, or by adding to a solution of pure sodium hydroxide an excess of bromine and evaporating to dryness; 9 grams of the powdered residue are dissolved in 100 c.c. of water and diluted to the requisite strength after a preliminary titration.

The actual determination of phenol is carried out as follows: 4 grams of the sample, or more if the amount of phenol present is small, is dissolved in or mixed with water, and made up to 1 litre. 25 c.c. of this solution, filtered if necessary, are placed in a bottle provided with a well fitting stopper, of about 400 c.c. capacity. 100 c.c. of the bromide and bromate solution are added, and then 5 c.c. of concentrated hydrochloric acid, in order to set free the bromine. The bottle is immediately closed, shaken and allowed to stand for 15 minutes. 10 c.c. of the potassium iodide solution are added and the whole is well mixed again. The free iodine liberated by the excess of bromine is estimated by titration with the thiosulphate solution, adding a few c.c. of the starch solution as indicator towards the end of the process.

If the standard solutions used are of the strength prescribed above, and the operations carried out as

[1] See footnote, p. 52. $2\,KI + Br_2 = 2\,KBr + I_2.$
$2\,Na_2S_2O_3 + I_2 = Na_2S_4O_6\ 2\,NaI.$

described, then the percentage of phenol in the sample is given by the formula

$$(2\,a - b) \times 0{\cdot}61753,$$

where $a$ = the number of cubic centimetres of thiosulphate solution required by 50 cc. of the bromide and bromate solution used, and $b$ the number of cubic centimetres required by the iodine equivalent to the final excess of bromine.

Care should be taken that the 25 c.c. of solution used for titration do not contain more than 0·1 gram of phenol.

*Phenol in mixtures with Cresols.*—For the approximate estimation of phenol in mixtures with cresols, the method of determining the solidifying point of the fraction distilling between 180° and 190° may be employed. (See under "Crude Carbolic Acid," p. 59.)

A modification of the above titration method is described in Chapter IV. (p. 148) for the determination of phenol and cresols in phenolic soaps.

### Crystallised Carbolic Acid. Tests for Purity.

Under this heading are described the determination of (*a*) the solidifying point, and (*b*) water.

(*a*) *Solidifying Point.*—This is the most important test for the purity of crystallised phenol. The purest phenol solidifies at 40·9°, while for pure phenol of commerce, it is usual to demand a solidifying point of 39° to 41°. The presence of cresols or water causes a lowering in the solidifying point. For the determination, Kraemer and Spilker give the following directions: an average sample of 50 grams, which has been taken from a large sample which has been liquefied and mixed with precautions for the exclusion of moisture, is allowed to

cool very slowly while it is constantly stirred with a thermometer, graduated in tenths of a degree ; when the solidifying point is reached, the thermometer should not be falling more than half a degree per minute. The solidifying point is the temperature at which a small crystal of phenol, introduced into the liquid, just begins to grow. If the cooling is carried too far, the temperature rises again when crystallisation sets in ; the highest point reached is the real solidifying point.

(*b*) *Water*.—This constituent may be determined in crystallised carbolic acid by mixing it with 5 times its weight of dry levigated lead oxide and drying at 70° to 80° until constant in weight. The function of the lead oxide is a mechanical one, the object of the admixture being to facilitate the evaporation of the water.

As little as 1 per cent. of water may be detected by the milkiness produced when the phenol is shaken with an equal volume of chloroform.

Crude carbolic acid, consisting either entirely of cresylic acid, *i.e.*, cresols, or of a mixture of the latter with phenol, is largely used for disinfecting purposes. Very often, cresylic acid is mixed with soft soap and water to form an emulsion, owing to its sparing solubility in water. The analysis of such preparations will be described in the chapter on soap. Pure phenol is used in medicine, and in the manufacture of dyes and picric acid.

## The Examination of Creosote Oil and its Products.

This portion of the coal tar distillate is a viscous, greenish-yellow fluorescent liquid which partially solidifies on cooling, owing to the separation of naphthalene. The solid matter amounts to some 20 per cent. Creosote oil has an average specific gravity of 1·04. Its principal constituents are naphthalene, which usually amounts to 20 to 30 per cent. or more, and higher phenols, including

cresols, xylenols, naphthols, etc., which amount to 10 to 20 per cent. In addition to these may be mentioned aniline, and other basic compounds such as acridine, cryptidines, and quinoline, and hydrocarbons such as methyl naphthalene, diphenyl, anthracene, acenaphtene, hydronaphthalenes, etc.

On redistillation, a little light oil and carbolic acid are separated, and the two main fractions obtained, *i.e.*, first and second naphthalene oils, are allowed to cool, and the naphthalene crystallising out is removed by filtration and further purified. The mother liquors contain varying proportions of naphthalene and other hydrocarbons, about 10 to 30 per cent. of phenols and smaller amounts of basic substances. The liquors obtained from the more volatile first naphthalene oil are used as disinfectants, sometimes by themselves, sometimes in the form of emulsions with soft soap, or mixed with lime, kieselguhr, borax, or other solid material. They may also be redistilled to yield a product containing about 50 per cent. of phenols which is mixed with zinc chloride solution to from an emulsion for pickling timber. The mother liquors form the second naphthalene oil, are also largely used for preserving timber, *i.e.*, harbour piers, railway sleepers, etc.

The preparations containing soap, such as creoline and lysol, are treated of in the chapter on Soap. Under the present heading the analysis of phenolic disinfecting powders, creosoting liquors and the testing of naphthalene for purity are described.

## The Examination of Phenolic Powders for Neutral Tar Oils and Phenols.

Different methods must be employed, (i.) for preparations made from powders which do not combine chemically with the phenols, such as borax or kieselguhr, and (ii.) for those made from lime or other basic substances forming salts with the phenols. As is well known, the phenols are neutralised by the oxides or hydroxides of the alkali metals or metals of the alkaline earths, but not by alkaline carbonates, borates, etc.

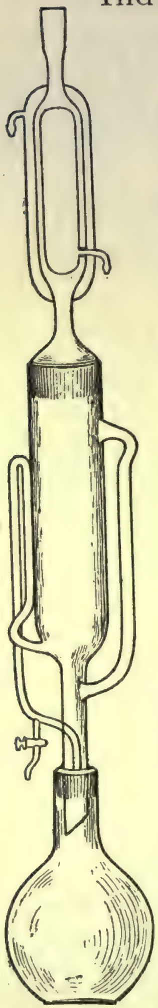


FIG. 7.—Soxhlet Extraction Apparatus with Davies Condenser.

(i.) *Preparations containing non-basic Powders.*—This, as well as the following method for powders with basic constituents, is taken from Allen's "Commercial Organic Analysis" (revised edition) :—

50 grams of the powder are placed in a thimble of filter paper and extracted with ether in a Soxhlet extraction apparatus, which is shown in the accompanying illustration. The three parts of the apparatus, *i.e.*, the flask, the extractor and the condenser, may be connected by corks or, better still, by means of ground glass joints. The solvent is placed in the flask below, and kept actively boiling on the water bath ; as it is condensed above, it falls back into the extractor and is automatically syphoned off as soon as it reaches a certain level. In this way the material is continually being exposed to the solvent action of fresh ether, while the dissolved material collects in the flask. The introduction of a tap in the lower part of the syphon bend is a useful modification due to Lewkowitsch ; by its means a small portion of the solvent may be withdrawn from time to time and evaporated to dryness ; when no residue is left,

the extraction process is known to be at an end. The ethereal solution which contains the phenol is shaken with 20 c.c. of a 20 per cent. solution of sodium hydroxide. (The amount of soda solution may be varied according to the amount of phenols supposed to be present, using 1 c.c. for each 1 per cent.) The ethereal solution is separated off, and the alkaline solution shaken out with two successive portions of ether, in order to extract the whole of the neutral tar oils. The united ether solutions are then shaken out with a small quantity of sodium hydroxide solution, in order to remove any traces of phenols which may remain with the neutral oils, evaporated in a tared flask on the water bath, and weighed, after drying at 100° C. for 1 hour.

The united alkaline solutions are boiled down in a flask to about 10 c.c. in volume, transferred to a graduated cylinder or burette, and acidified with dilute sulphuric acid containing 1 part of the concentrated acid to 3 parts of water. When the mixture is quite cold the volume of the separated phenols is read off, the weight being estimated on the assumption that 1 c.c. weighs 1·050 grams. If the presence of fatty or resin acids is suspected, the contents of the burette are transferred to a flask and submitted to steam distillation; the phenols will pass over the distillate, while the acids will remain in the flask. The latter may be characterised by their solubility in sodium carbonate solution.

(ii.) *Preparations containing Basic Powders.*—50 grams of the alkaline powder are mixed in a mortar with 5 c.c. of water, after which strong sulphuric acid is added, drop by drop, at intervals and mixed well into the powder or paste by means of a pestle; the addition of the acid should extend over several hours, in order to avoid a sensible rise in temperature; it is continued until the

whole mass is distinctly acid. If the resulting product is a paste, it is mixed with sufficient sand to bring it into a granular form; it is then extracted with ether in the Soxhlet apparatus, and the extract is submitted to the same treatment as described above for non-alkaline powders.

According to Allen, good powders should contain from 12 to 18 per cent. of phenols. It is doubtful whether powders containing lime are as efficient for disinfecting purposes as those in which the phenols are present in the free state.

## THE TESTING OF CREOSOTING LIQUOR.

Most of the creosote oil distilled is used for preserving timber which is to be used for railway sleepers, telegraph poles, harbour piers, etc. The basic constituents of the oil are believed to be of as much value as the phenols as antiseptics, and, moreover, they are said to form resin-like combinations with the phenols and unsaturated hydrocarbons, which fill up the pores of the wood and protect it from destruction by micro-organisms. Extensive adulteration with lignite, shale and rosin oils, which contain no bases, is therefore objectionable. The naphthalene and other neutral constituents are also believed to be beneficial, for, being introduced into the wood in a liquid state at about 50°, they solidify in the pores and form a protective covering throughout.

In testing creosoting liquor it is often necessary to adhere to a method described in a contract in which are stated the conditions which the article must fulfil. With such a complex mixture as creosoting liquor, the analytical results often vary considerably with slight variations in the method of analysis, and must therefore be judged with due regard to the process by which they have been obtained.

The following is a condensed extract of Tidy's specification:—

(1) "The creosote oil must be completely liquid at 38° C., no deposit taking place until it is cooled to 35° C."

(This brings the percentage of naphthalene and other solid hydrocarbons within certain limits.)

(2) "It must contain at least 25 per cent. of constituents not distilling over at (or below) 316° C.

(3) "Tested by the process described below, it shall show a total of not less than 8 per cent. of tar acids (phenols).

(4) "It shall contain no admixture of bone oil, shale oil, or any substance not derived from coal tar."

*The Determination of the Coal Tar Acids* (*Phenols*).—100 c.c. of the well mixed creosote is distilled at a temperature of 316° till there is no further distillate. The distillate is mixed and well shaken in a stoppered flask with a solution of sodium hydroxide of specific gravity 1·200; the mixture is heated on the water bath and then, after the stopper has been replaced, shaken vigorously for 1 minute. The contents of the flask are poured into a separating funnel, and the soda solution is drawn off when the layers have separated. The creosote is heated a second and a third time with fresh portions of 20 c.c. of the soda solution, the process being repeated just as described. The three soda solutions are mixed, and when cold, any particles of oily matter are got rid of by the use of a separating funnel; the solution is then boiled vigorously to expel the last traces of neutral or basic oil. On cooling, dilute sulphuric acid is added (1 part acid to 3 of water) until the whole is slightly acid, and the mixture is transferred to a separating funnel and allowed to stand to cool until the tar acids have separated. The latter are now separated off and dissolved in 20 c.c. of soda solution of the same strength as that used before, and 10 c.c. of water; the alkaline solution is well cooled, transferred to a 100 c.c. measure and acidified with dilute sulphuric acid (1 to 3), of which about 35 c.c. will be sufficient. The whole is allowed

to stand for 2 hours to cool, after which the volume of the tar acids is read off.

Instead of distilling the creosote to 316°, Sadtler prefers to distil to the point of pitching, and thus includes some of the higher phenols in the estimation, which are rejected along with the still residue in Tidy's process; in view of the fact that the higher phenols are in all probability just as efficacious in the preserving of timber as the lower members of the series, this modification would seem to be desirable. Further, in extracting the phenols, Sadtler recommends the use of 10 per cent. sodium hydroxide solution at first, followed by successive portions of 30 per cent. solution in the subsequent extractions, until all the phenols have been dissolved out. In order to get a good separation, petroleum ether may be added; the separation of the last traces of neutral oils is also facilitated by the use of this solvent, which may be completely removed by subsequently boiling the alkaline solution.

*Estimation of the Basic Constituents.*—The following method is due to Sadtler: 100 c.c. of the creosote oil are distilled from a retort to the point of coking, and the distillate is agitated with two successive portions of 20 c.c. of dilute sulphuric acid (1 to 3). The acid solution which contains the bases in the form of sulphates is separated off and rendered alkaline by the addition of sodium hydroxide solution. The bases are liberated, partly in the form of an oily layer, and partly in aqueous solution. The oily layer is separated off, and the alkaline liquid is distilled nearly to dryness. The distillate is mixed with the oily extract and the whole is acidified with hydrochloric acid, and evaporated to dryness on the water bath. The residue, which consists of the hydrochlorides of the tar bases, is dissolved in a

small quantity of water, and solid sodium hydroxide is dissolved in the liquid till a saturated solution is obtained. The bases may then be separated, weighed, and, if desired, further examined by conversion into platinichlorides. They may, however, be more conveniently estimated by the following titration process (Bureau of Animal Industry, Bulletin 107, U.S. Dept. of Agriculture), which was originally devised for the estimation of tar bases in sheep dips. (See Chapter IV.)

The acid solution of the bases is filtered if necessary, made up to 300 c.c. with water, and divided into two equal portions in two similar titration flasks of about 300 c.c. capacity. To the contents of one of these flasks is added a drop or two of methyl orange solution, and then semi-normal sodium hydroxide solution until the red tint just disappears, as nearly as can be judged by comparison with the other portion which has been treated with an equal amount of methyl orange. 0·1 to 0·2 c.c. of semi-normal soda solution are then added. This first titration is not quantitative, but is carried out to obtain a standard by which the second portion may be titrated to neutrality.

A neutral solution of the chlorides or sulphates of the bases is thus obtained; any further addition of alkali would produce an alkaline reaction with the methyl orange. Phenol phthalein is now added, and titration is continued to the end point of this indicator; the reason why an alkaline reaction is not observed immediately is that the alkali displaces the tar bases from combination with the mineral acids, and the liberated bases have no action on the phenol phthalein; only when the whole of the bases has been liberated will the alkali added produce a coloration with the phenol phthalein. The number of cubic centimetres

of soda solution used between the two indicators, multiplied by 0·079, gives the total amount of the bases in terms of pyridine, or, multiplied by 0·129, in terms of quinoline.

## NAPHTHALENE.

This substance occurs in coal tar to the extent of 5 to 10 per cent., being one of its chief constituents. In the dyeing industry it is of great importance as the source of the naphthols, naphthylamine, phthalic acid, etc. As mentioned above, naphthalene is obtained from the carbolic oil and creosote oil fractions of coal tar ; it is freed from phenols by washing with caustic alkali solution, and sometimes with sulphuric acid, which removes the phenols as sulphonic acids. Further purification is effected by filter-pressing the warm material, and fractional distillation.

*The Testing of Naphthalene for Purity.*—Naphthalene which is to be chemically treated is required to be as pure as possible. The purest naphthalene melts at 79·5° to 79·8° and boils at 217° to 218° at 760 mm. pressure. The following tests for purity may be applied to commercial naphthalene :—

(1) Dissolve in hot pure concentrated sulphuric acid ; the solution should turn only faintly purple or pink. With less pure brands it will turn red.

(2) Pour pure fuming nitric acid on to the bottom of a desiccator, and place the naphthalene in a watch glass above it, covering up the whole as usual ; if the sample remains white for half an hour it is good, and if for 2 hours, it is excellent. Inferior qualities soon turn pink. After some hours, all samples go yellow, probably owing to the formation of nitronaphthalene.

(3) Phenols may be tested for by boiling the sample with dilute sodium hydroxide solution, cooling, filtering and adding to the filtrate a little bromine water and

dilute hydrochloric acid; any phenols which may be present will be precipitated as bromine derivatives.

(4) Quinoline bases may be tested for by dissolving the sample in concentrated sulphuric acid, pouring the solution into water and filtering; on making the filtrate alkaline and distilling, the bases will pass over with the steam and be recognisable by their characteristic smell.

For naphthalene which is to be used as insecticide or for carburetting gas, the tests for purity need not be so stringent.

## Anthracene Oil Products.

Anthracene oil, which is distilled from about 270° to the point of pitching, is a greenish yellow fluid, turning brown on exposure to air, and boiling from 280° to 400°. On cooling to the ordinary temperature it becomes semi-solid, yielding a crystalline deposit of crude anthracene, amounting to about 30 per cent. of the total. Crude anthracene is an exceedingly complex mixture; in addition to many substances of unknown constitution, it contains the following: naphthalene and homologues, anthracene, methyl anthracene, etc., phenanthrene, acenaphtene, diphenyl, pyrene, fluorene and other hydrocarbons of high molecular weight, phenols of complex constitution, and nitrogen compounds such as cabazole, acridine and imidophenyl naphthyl. The fluid portions of the anthracene oil are of little value; they are either redistilled or used as lubricants. The solid constituents are worked up for anthracene, which is one of the most valuable constituents of coal tar, being the basis of the alizarin dyes. It is present in coal tar to the extent of about 0·3 to 0·9 per cent., and constitutes from 2½ to 3½ per cent. of the anthracene oil. The other constituents of anthracene oil, with the exception of carbazole, are of little or no commercial importance.

After pressing, first cold and then hot, a crude anthracene cake containing some 30 to 40 per cent. of anthra-

cene is obtained. A second crop, crystallised from the anthracene oil at about 15°, yields an anthracene cake containing 10 per cent. of anthracene. The subsequent processes by which pure anthracene is obtained consist mainly in washing the finely divided product with solvents such as naphtha, creosote oil, acetone or liquid sulphur dioxide.

## The Examination of Crude or Purified Anthracene.

The value of the product depends, firstly, on the amount of real anthracene it contains, and secondly, on its freedom from undesirable impurities, the chief of which are the higher paraffins and methyl anthracene, which are often present in appreciable quantities in some tars, notably those from Scotland and the north of England. These impurities are very difficult to remove, and if present in appreciable quantities, render the anthracene unfit for alizarin making; the paraffins especially impede the oxidation to anthraquinone, and render the purification of the latter difficult. Carbazole is another objectionable impurity which should be removed as completely as possible. The estimation of anthracene and the detection and estimation of the impurities just mentioned are described below.

Crude unwashed anthracene cake formerly contained about 30 to 40 per cent. of anthracene, but in recent years it has been found possible to obtain a product containing already at this stage from 40 to 50 per cent., or even more, of anthracene.

*The Estimation of Anthracene in Crude or Purified Anthracene Cake.*—The method usually adopted is known as the "Höchst test," in which the anthracene is quantitatively oxidised to anthraquinone, by means of chromic acid in acetic acid solution, and estimated as such. During the process practically all the accompanying substances are either completely oxidised or converted

into products which are easily removed by washing with water or dilute alkaline solution. In order that reliable results may be obtained, the following directions should be closely adhered to :—

1 gram of the carefully sampled anthracene cake is treated with 45 c.c. of pure glacial acetic acid in a 500 c.c. flask, fitted with a reflux condenser, and the mixture is kept boiling while a solution of 15 grams of pure chromic acid in 10 c.c. of glacial acetic acid and 10 c.c. of water is added drop by drop ; the addition of this oxidising mixture is to extend over 2 hours, after which the boiling is continued for 2 hours more. The mixture is then allowed to stand for 12 hours, when 400 c.c. of cold water are added. After another 3 hours, the precipitated anthraquinone is collected on a filter and washed, first with distilled water, then with 200 c.c. of a boiling 1 per cent. solution of potassium hydroxide, and finally with hot distilled water. The quinone is then transferred, with the aid of a wash bottle, to a dish, dried at 100°, and treated with 10 c.c. of fuming sulphuric acid at 100° for 10 minutes on the water bath. The solution thus obtained is poured into a flat dish and kept for 12 hours in a moist atmosphere, say, on a thick layer of moist blotting paper under a bell jar, to absorb water. 200 c.c. of cold water are then added to the contents of the dish ; the precipitated anthraquinone is collected on a filter, and washed, first with distilled water, then with boiling 1 per cent. potassium hydroxide solution, and finally with hot distilled water. The residue on the filter is transferred to a platinum dish, dried and weighed ; after volatilising the quinone at a gentle heat, the dish is re-weighed with the particles of ash and coal which remain. The difference between the two weights is equal to the weight of the anthraquinone, which,

multiplied by 0·8558, is equal to the weight of real anthracene in the sample.

The anthraquinone got by the above process should be crystalline, and of a pale yellow colour. An orange or red colour indicates the presence of the quinones of other hydrocarbons, especially those of phenanthrene or chrysene, the latter being recognisable by the indigo coloration which it produces on the addition of concentrated sulphuric acid. The quinone of imido phenyl naphthyl prevents the crystallisation of the anthraquinone; according to Allen, it may be destroyed by longer heating with fuming sulphuric acid. In the presence of methyl anthracene the anthraquinone obtained does not show the usual characteristic needles, but it is more or less felted.

Carbazole,[1] like imido phenyl naphthyl,[2] produces a quinone which interferes with the purification of the anthraquinone; according to Behrens, it is detected by extracting the anthracene with cold ethyl acetate, evaporating the solvent on a watch glass and warming with a few drops of nitrobenzene and phenanthraquinone; characteristic narrow plates of a coppery lustre are got if carbazole is present.

*Estimation of Carbazole.*—This substance, which occurs in coal tar to about the same extent as anthracene, has lately become of some importance as raw material in the cyanide industry, as well as in the manufacture of dyes. Owing to the weakly acidic nature of the imido group which it contains, it may be separated from the accompanying constituents by heating with potash, when a potassium derivative is formed.

[1] $C_6H_4$——$C_6H_4$
NH

[2] $C_6H_4$——$C_{10}H_6$
NH

For its estimation, Kraemer and Spilker recommend the following process: the crude anthracene, in a finely divided state, is extracted with warm dilute sulphuric acid, which removes all other nitrogen compounds which are of a basic nature. The nitrogen is then estimated in the residue by Kjeldahl's process (see p. 22) and calculated to carbazole.

*The Determination of Paraffins in Crude Anthracene.*—Kraemer and Spilker recommend the following process, which, in theory, is the same as their process for estimating paraffins in benzol (see p. 51): 10 grams of the finely powdered anthracene are shaken with 70 c.c. of ether in a 100 c.c. measuring flask for 10 minutes, the flask is filled to the mark with ether, and the contents are allowed to settle. 50 c.c. of the clear solution, representing 5 grams of the sample, are introduced into a porcelain dish, the ether is allowed to evaporate, and the residue is dried at 100° for half an hour. After cooling, it is triturated with 8 c.c. of fuming sulphuric acid, containing 20 per cent. of $SO_3$. The dish is covered with a watch glass and heated to 100° for 3 hours, with frequent stirring. The contents are then washed into a beaker with 500 c.c. of hot water and, after cooling, passed through a dry filter. The beaker is rinsed out on to the filter, which is washed with water until barium chloride solution no longer produces a precipitate in the filtrate; the filter is then allowed to drain, thoroughly moistened with absolute alcohol, and the paraffin is washed by means of ether into a weighed dish until a few drops of the running ether leave no residue on evaporation. The last traces of paraffin are removed from the beaker by means of ether, which is also passed through the filter and added to the main portion. The total ether solution is evaporated in the dish, the

residue dried at 105° for 2 hours, and weighed as paraffin.

Good anthracenes should contain little or no paraffin ; inferior qualities may, however, contain about 4 to 6 per cent. of this constituent.

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## CHAPTER III

### THE FATTY OILS AND FATS

### INTRODUCTORY.

THE fatty oils and fats constitute, from the chemical point of view, a well defined group of naturally occurring products. Consisting essentially of mixtures of the mixed or simple neutral glycerol esters of the aliphatic acids and other acids belonging to allied series, they may be hydrolysed by the action of caustic alkali with the formation of free glycerol and the potassium or sodium salts of the fatty acids ; when the aqueous solutions of these salts, which are generally known as soaps, are acidified with mineral acid, the bulk of the fatty acids are precipitated.

The acids which are most commonly met with in the saponification products of the oils and fats are as follows :—

(1) The aliphatic acids containing an even number of carbon atoms from butyric acid, $C_4H_8O_2$, to arachidic acid, $C_{20}H_{40}O_2$.

(2) Unsaturated open chain acids yielding dibromo additive compounds, of which the more well-known are oleic acid, $C_{18}H_{34}O_2$ $(CH_3(CH_2)_7CH = CH(CH_2)_7COOH)$; rapic acid, $C_{18}H_{34}O_2$; and erucic acid, $C_{22}H_{42}O_2$

$$(C_8H_{17} - CH = CH(CH_2)_{11}COOH).$$

(3) Unsaturated acids yielding tetrabromo additive compounds, of which one of the most well-known is linolic acid, $C_{18}H_{32}O_2$.

(4) Acids yielding hexabromo additive compounds, of which the most well-known is linolenic acid, $C_{18}H_{30}O_2$.

(5) Acids yielding octobromo additive compounds, *e.g.*, clupadonic acid, $C_{18}H_{28}O_2$.

In addition to the above, higher or lower aliphatic acids than those mentioned, acids containing uneven numbers of carbon atoms in the molecule, cyclic unsaturated acids and hydroxy acids may be met with in small quantities or in isolated cases. The chemical constitution of many of the acids obtained from the oils and fats is, as yet, doubtful.

By far the greater number of the fatty oils and fats are complex mixtures from which it is generally extremely difficult to isolate chemical individuals; many of the methods for their examination and identification are therefore methods for determining the mean of certain chemical or physical characteristics of their constituents or of the mixtures of fatty acids which have been obtained from them by certain standard methods. Under this heading come the so-called "quantitative reactions" such as the determination of the iodine absorbing power and the saponification value, which are described below. Chemical methods of a more definite nature may, however, be employed in certain cases; as an example may be mentioned the examination of the small amounts of unsaponifiable matter which are present in all fatty oils and fats. The vegetable oils and fats, or at least all the more commonly known members of this group, contain small amounts of an easily recognised substance known as phytosterol, which is absent from all animal fats; the latter, on the other hand, contain small amounts of cholesterol, which is absent from the vegetable products. Another example is seen in the isolation of arachidic acid from arachis oil. The colour tests, such as those employed for the recognition of sesame and cotton-seed oils, depend on the detection of small amounts of characteristic constituents of these oils by chemical means.

All fatty oils and fats naturally contain smaller or larger amounts of free fatty acids, presumably produced by the partial hydrolysis of the glycerides; in oils and fats of animal origin the proportion of free acids is normally very small; in vegetable oils and fats it is

generally larger, an extreme case being that of palm oil, which may contain from 10 to 80 per cent. of free fatty acids. One of the principal objects of the refining processes to which vegetable oils and fats are submitted is the removal of these free acids by treatment with limited amounts of alkali; such processes are, however, only undertaken in the case of products in which the amounts of free acids are normally confined within reasonable limits.

All fatty oils and fats, especially those of vegetable origin, develop acidity on keeping, unless protected from light, air and moisture; in the opinion of Lewkowitsch, this is in a large measure to be ascribed to the action of hydrolysing enzymes which become active under certain conditions. The vegetable oils and fats are usually stored as reserve food material in seeds and fruits, and are accompanied by enzymes, the function of which is to convert them into soluble material which can be assimilated by the growing plant. Lewkowitsch ascribes the development of rancidity to the combined action of air and light on the free acids so produced.

*Classification of the Fatty Oils and Fats.*—Complex naturally occurring substances such as the fatty oils and fats cannot, of course, be submitted to any hard and fast rigid system of classification. The system adopted by Lewkowitsch, given below, is based partly on the origin of the product and partly on the drying power, *i.e.*, the power of absorbing oxygen with the formation of more or less viscous products. This important property depends on the proportion of unsaturated acid radicles present as well as on the degree of unsaturation of the latter; the combined effect of these chemical characteristics is accurately measured by iodine absorbing power, or, as it is generally called, the "iodine value" of the oil or fat. As pointed out by Lewkowitsch, the iodine value is the most convenient constant on which to base a system of classification, as on it depend to a large extent important physical properties, notably the consistence, melting and solidifying points.

The following scheme of classification should be compared with the table of constants and characteristics given on p. 106 :—

1.—*Liquid Fats.*

(A) Vegetable oils.
- (*a*) Drying, *e.g.*, linseed and hempseed oils.
- (*b*) Semi-drying, *e.g.*, soya bean, cotton seed, rape seed, and sesame oils.
- (*c*) Non-drying, *e.g.*, arachis, olive and castor oils.

(B) Animal oils.
- (1) Marine animal oils.
  - (*a*) Fish oils, *e.g.*, menhaden oil.
  - (*b*) Liver oils, *e.g.*, cod liver oil.
  - (*c*) Blubber oils, *e.g.*, seal and whale oils.
- (2) Terrestrial animal oils, *e.g.*, sheep's foot and neat's foot oils.

2.—*Solid Fats.*

(A) Vegetable fats, *e.g.*, palm oil, cacao butter, palm nut and cocoanut oils.

(B) Animal fats.
- (*a*) Drying fats.
- (*b*) Semi-drying fats.
- (*c*) Non-drying fats, *e.g.*, beef tallow, mutton tallow, butter fat.

The various groups in this system of classification are, of course, by no means sharply defined, for all gradations in drying power and consistence are met with amongst the oils and fats.

## The Estimation of Fatty Matter in Seeds, Oil-cake, etc.

Vegetable oils and fats are obtained from seeds, fruits, etc., by submitting the disintegrated material to high pressure, either hot or cold, the finer, edible fats usually being expressed at the ordinary temperature. In recent years processes involving the extraction of fatty material by means of organic solvents have been introduced.

The exhausted material, known as oilcake, which usually contains from 6 to 16 per cent. of fat and varying proportions of nitrogenous matter, is largely used as fodder for cattle.

The method to be described is generally applicable for the determination of fatty matter in oleaginous seeds or fruits such as rape seed, linseed, soya beans, copra (*i.e.*, dried cocoanut endosperm), etc., oilcake, flour and similar food materials.

If the material contains much water, it must first be dried at a gentle heat; complete drying is only necessary if ether is to be used as the extracting solvent (see below); if any of the other solvents mentioned below are to be used a rough drying will be sufficient. For the determination, 100 grams of material may be taken. It is prepared for extraction with an organic solvent in the Soxhlet apparatus (see p. 66), by disintegrating in a food-mincing machine or hand mill, and then triturating with ignited sand in a mortar, in order that the vegetable tissue may be thoroughly broken up. If, however, the material contains so much fat that it forms a pasty mass during the latter process, it should be submitted to a preliminary extraction in the Soxhlet apparatus after having been roughly broken up in the mincing machine or mill, then triturated with sand in a mortar, and re-extracted. The following solvents may be used for extracting the fat: ether, petroleum ether which is completely volatile below 80°, carbon tetrachloride or trichloro ethylene. It should be noted that as ether is miscible to a certain extent with water, it may extract constituents other than fat unless the material has been thoroughly dried. The other solvents mentioned have not this disadvantage. The two last mentioned solvents have the advantage of being non-inflammable; trichloro

ethylene, however, is especially liable to decompose with evolution of hydrochloric acid if exposed to light for any length of time in presence of traces of moisture.

On the whole, therefore, petroleum ether may be regarded as the most suitable extracting medium for the present purpose.

The process of extraction will require several hours; if great accuracy is desired, it may often be advisable to triturate the exhausted material with sand a second time and submit it to further treatment in the Soxhlet apparatus. The fat in the flask is freed from the solvent by distillation and heating to 105° in an oven, and weighed.

The crude fatty matter thus obtained may be analysed for its content of free fatty acids as described under "Acid Value," and compared in this respect with a refined sample of the same product. If it is required for further examination, such as the determination of its iodine value, especial care must be taken to free it completely from the solvent used in the extraction process, at the same time avoiding prolonged exposure to air at an elevated temperature; the latter treatment may give rise to appreciable oxidation of fats having high iodine values. After most of the solvent has been removed by distillation, the fat may be heated under reduced pressure to the temperature of boiling water till all traces of the solvent and water have been removed.

## The Examination of the Fatty Oils and Fats.

*Preparation of the Sample.*—Before the sample is submitted to a chemical and physical investigation, it must be freed from foreign matter such as water, dissolved soaps, vegetable or animal tissues, etc. In most cases it will be sufficient to melt the sample, and, if water is

seen to be present, allow it to stand in a warm place till separation has taken place, when the clear fat is passed through a dry filter. Dissolved mineral matter such as soap is detected by burning off a portion of the sample and examining the residue, if any, for metals ; it may be removed by extracting the melted fat with dilute nitric acid and after washing with warm water, proceeding as directed above. Foreign matter such as paraffin, rosin oil, etc., is not removed at this stage, and is only detected on closer examination.

The sample should always be thoroughly liquefied, at a gentle heat if necessary, and well mixed when portions of it are to be abstracted for analysis or physical determinations ; it will be found that oils often deposit small quantities of solid matter at the ordinary temperature, which sink to the bottom of the vessel, while solid fats, when cooled slowly, first deposit their higher melting glycerides, so that the composition of the solidified mass may not be entirely uniform.

*Estimation of Water in Fats.*—This determination is of especial importance in the case of butter and margarine, in which the water and fats are mixed so as to form emulsions. The determination may be carried out as follows : about 20 grams of dried pumice in small lumps are weighed in a flat dish, and about 10 grams of a fair average sample are added. The whole is then weighed and dried in an air oven at 110° till constant in weight. The drying will take about 2 hours, and should not be unduly prolonged, as an increase in weight will then take place owing to the oxidation of the fat. The loss in weight of the sample represents the water.

According to the Sale of Butter Regulations of 1902, the percentage of water in butter is limited to 16 per cent. Similarly, margarine containing more than 16 per cent.

of water would be held to be not genuine margarine but margarine and water.

## The Physical and Chemical Constants of the Fatty Oils and Fats.

Before describing the methods for determining the physical and chemical constants by which the various oils and fats may be recognised and quantitatively estimated, it should be pointed out that these constants, which are set out for the more well-known members of the group on p. 106, are not in the strict sense of the term constant for different samples of the same kind of oil or fat, but are liable to vary to a certain extent with such factors as the age, the race or strain of the animal or plant from which they were obtained, general treatment, nature of food or soil, climatic conditions, etc. Having regard to these variations, which will generally not be large enough to cause any serious error in the cases to be dealt with here, it will be realised that a certain amount of caution must always be exercised in basing conclusions on the results of the determination of such constants as the iodine and saponification values, specific gravity, etc. The acid value will be influenced, not only by the factors just mentioned, but also by the age and previous history of the particular sample under examination. The amount of unsaponifiable matter will, of course, be largely influenced by the addition of such substances as paraffin.

Some of the more important methods for examining fatty oils and fats are described below, after which follow a number of examples to illustrate how these methods may be applied in identifying the commoner fatty oils and fats, and analysing simple mixtures of the latter.

## Physical Methods for Examining Fatty Oils and Fats.

The physical methods available for the examination of fatty oils and fats will only be briefly dealt with, as

more definite information can generally be obtained by the use of chemical methods. Useful indications may sometimes be obtained from the specific gravity, melting point, refractive index, and sometimes also the optical rotation. Methods for determining the two first-mentioned constants are described below, and also the "titer test" or solidifying point of the mixed fatty acids derived from the fat. The latter test is generally of greater value for purposes of characterisation than the determination of the melting point of the fat itself.

(*a*) *Specific Gravity*.—This determination may be carried out by means of the Sprengel pyknometer or the ordinary specific gravity bottle; in most cases, however, sufficiently accurate results may be obtained by use of the Westphal balance which is described on p. 42. In case of oils which are completely liquid at the ordinary temperature, the specific gravity is taken at 15·5°, and in case of solid fats, at the temperature of boiling water. If it is only necessary to heat the fat a few degrees above 15·5° for complete liquefaction, the determination may be made at this temperature, and the result reduced to 15·5°. Allen gives the mean temperature correction for most common fatty oils and fats, with the exception of whale oil, as 0·00064 per degree Centigrade. The specific gravities of the common oils and fats are set out in the table on p. 106. In some cases the specific gravity may furnish useful indications in detecting adulterations.

For more complete descriptions of methods for determining the specific gravities of oils and fats see the works mentioned at the end of this chapter.

(*b*) *Melting Point*.—The methods commonly used for relatively pure organic substances cannot be applied to fats. Numerous methods have been designed for determining the melting points of fats, and as varying results are obtained according to the method used, it is not

advisable to place too much reliance on indications afforded by comparison of results obtained with figures given in the literature. The following method, elaborated by Blichfeldt for the testing of edible fats and fatty mixtures, may be recommended as being expeditious and capable of yielding trustworthy results if properly carried out.

Into one end of a glass tube, 7 cm. long, 1 mm. bore and 2 mm. outside diameter, is introduced a column of the melted fat, 1 cm. long. The fat is suddenly solidified by placing the tube between two flat pieces of ice, so that the length containing the fat is well covered. After having been kept on ice for at least two hours, so that the fat may have thoroughly set, the tube is placed in a water bath so that the top of the fat column comes 1 cm. below the surface; while the water is kept well stirred, the temperature, as indicated by a delicate thermometer, is raised at the rate of about 1° per minute; the temperature at which the fat becomes sufficiently soft to be forced up the tube by hydrostatic pressure is taken as the melting point. If only one or two melting points are to be determined, the tubes may be attached to the thermometer bulb by a rubber band. If a number of tests are to be carried out simultaneously, the tubes may be held in position in shallow grooves in a long strip of wood by means of a wide rubber band which is wired down at several points throughout the length of the strip. The temperature of the water bath must be raised gradually and evenly, the heat being supplied not by a direct flame, but by immersing in a second water bath kept at a slightly higher temperature. The stirring should be carried out so as to cause a constant current of water to circulate past the melting point tubes and thermometer.

Many fats show perfectly sharp melting points by the

above methods, duplicate tests agreeing within 0·2°, or at the most 0·3°. In the case of some animal fats or mixtures of these with oil, especially where the proportion of stearin to oil is small, the melting points observed are less sharp, the movement of the fat up the tube being sluggish.

(c) *The Titer Test.*—By the titer test is understood the determination of the solidifying point of the insoluble fatty acids, together with the small amount of naturally occurring unsaponifiable matter, as obtained by the process now to be described. The procedure set out is that recommended by Lewkowitsch.

Saponify 100 grams of the oil or fat by boiling with 40 c.c. of aqueous potassium hydroxide solution of specific gravity 1·4, and 410 c.c. of alcohol, in a porcelain dish on a water bath, stirring continually until the soap becomes pasty. Dissolve the residual soap in 1,000 c.c. of water and boil until all the alcohol has been removed, replacing the water which has evaporated, from time to time. Decompose the soap solution by acidification with dilute sulphuric acid and when, by continued boiling, the fatty acids have been obtained as a clear layer floating on the aqueous liquid, draw off the latter by means of a syphon, and wash the fatty acids several times with hot distilled water until all acid, as tested for by methyl orange, has been removed. Place the dish with the fatty acids on the water bath until the latter are melted, and the water and impurities have settled out; after passing through a fluted filter in a heated funnel, they will be sufficiently dry for further examination. The actual determination may be carried out by the following method, due to Dalican and recommended by Lewkowitsch:—

The mixture of fatty acids, after standing overnight in

a desiccator, is carefully melted in an air bath, and as much of it is poured into a test tube 16 cm. long and 3·5 cm. wide as will fill the tube somewhat more than half full. The tube is fitted by means of a cork into a wide mouth bottle, 10 cm. wide and 13 cm. high; and an accurately standarised thermometer, graduated in tenths of a degree, from 0° to 60° C., having a mercury bulb, 3 cm. long and 6 mm. in diameter, is placed so that the bulb is in the centre of the mass of the fatty acids. When a few crystals appear at the bottom of the tube, the mass is stirred by giving the thermometer a rotatory movement, first three times from right to left and then three times from the left to right. The mass is then stirred continually with a quick circular movement of the thermometer without allowing it to touch the sides of the vessel, and taking care that all the solidified portions, as long as they form, are well stirred into the mass until it has become cloudy throughout. At this point the thermometer is carefully observed; at first the mercury will fall or remain stationary, after which it will suddenly rise some tenths of a degree, remain stationary for a short time and then fall again. The maximum temperature attained during this rise is the titer or solidifying point of the mixed fatty acids.

The above method is stated by Lewkowitsch to give very concordant results; it follows, of course, that attention must be paid to detail, especially in the actual determination of the solidifying point.

The titer test is largely used for the commercial valuation of fats used in soap and candle making, notably tallow and palm oil. It is customary to stipulate that the solidifying point shall not lie below a certain value, say, 43·5° C. in the case of beef tallow, and to reject the material or make a deduction in the price paid for it if it fails to comply with this standard.

Reference to the table on p. 106 will show that the mixed fatty acids derived from various oils and fats may, in some cases, readily be distinguished from one another by means of the titer test; thus, compare the figures given for cotton seed oil and rape seed oil. This circumstance may be made use of in the examination of fatty oils and fats in mixtures with mineral oils, it being possible to separate the fatty acids from such mixtures, but not the fatty oils or fats themselves. This problem will be further discussed under the examination of lubricating oils. (Chapter V.)

## Chemical Methods for Examining Fatty Oils and Fats.

Under this heading will be described the determination of (*a*) the iodine value, (*b*) the saponification value, and (*c*) the Reichert-Wollny value. These may be considered as being, within certain limits, constants for the individual fatty oils and fats, and may often be employed as a basis for their identification and approximate estimation in mixtures. In addition will be described the determination of (*d*) the acid value, and (*e*) the unsaponifiable matter. The former of these may, as explained above, vary with the age and previous history of the sample, and cannot be looked on as a constant to be used for the purposes of identification. The amount of unsaponifiable matter is normally small in most of the common fatty oils and fats, and its quantitative determination is generally of no great importance, except in cases where the presence of added foreign material is suspected. The qualitative examination of this constituent, also to be described below, is, however, of some importance in the differentiation of animal and vegetable fats, and especially in the detection of the latter as adulterants in the former. (See "Phytosteryl Acetate Test.")

(*a*) *Iodine Value.*—The iodine value expresses the number of parts by weight of iodine which can be absorbed by 100 parts of the fat. In Hübl's original

process the fat was treated with iodine in an alcoholic solution containing mercuric chloride. In Wijs' process, which is described below, a solution of iodine monochloride in glacial acetic acid is used, the time required for absorption being considerably shorter than in Hübl's process.

In the determination a weighed quantity of the fat, dissolved in carbon tetrachloride, is treated at the ordinary temperature with a definite volume of the iodine monochloride solution, and an equal volume of the latter is set aside at the same time, under similar conditions, as a blank test. After the requisite time has elapsed the iodine monochloride is estimated in each case by titration with sodium thiosulphate solution. The difference in the number of c.c. required in the blank test and in the actual determination is calculated to express the percentage proportion of iodine absorbed by the fat.

The following solutions will be required :—

*Iodine Monochloride Solution.*—A 10 gram tube of iodine trichloride and 11·1 grams of iodine are separately dissolved in pure glacial acetic acid, avoiding absorption of moisture. The two solutions are mixed and made up to 1,500 c.c. with pure glacial acetic acid (Kahlbaum's 99 to 100 per cent. may be used). The resulting iodine monochloride solution must be preserved in well-stoppered bottles to avoid access of moisture.

*Sodium Thiosulphate Solution.*—24 grams of the crystallised salt are dissolved in water and made up to 1,000 c.c. This solution may be conveniently standardised by the following method, due to Volhardt: 3·8631 grams of pure potassium dichromate, free from the sodium salt, are dissolved in water and made up to 1,000 c.c. 10 c.c. of a 10 per cent. solution of potassium iodide solution and 5 c.c. of hydrochloric acid are placed

in a stoppered bottle and exactly 20 c.c. of the dichromate solution are run in. The resulting mixture now contains exactly 0·2 gram of free iodine, which may be titrated with the sodium thiosulphate solution, using starch as an indicator, towards the end of the process. The iodine equivalent of the thiosulphate solution may then be calculated.

*Starch Solution.*—About 1 part of starch is stirred up in 100 parts of water, and the mixture heated to boiling.

*Potassium Iodide Solution.*—A 10 per cent. solution of the pure salt in water.

To determine the iodine value, the fat is weighed out in a small specimen tube which is then dropped into a narrow mouthed bottle of about 500 c.c. capacity, and furnished with a well-fitting stopper. The amount of fat to be taken varies with its power of absorbing iodine; in the case of a drying oil, about 0·15 gram should be taken, but with a solid fat, having a low iodine value, such as cocoanut oil, the amount may be increased to about 1·5 gram. In any case, the amount of fat taken should be so regulated that the excess of iodine monochloride present after absorption is complete is more than half of the amount originally present. The fat is dissolved in 10 c.c. of carbon tetrachloride, and 25 c.c. of the iodine monochloride solution are run in from a pipette; in measuring out the solution for the blank test and for any other determinations which are to be made simultaneously, the same pipette should be used and allowed to empty itself in the same manner and drain for the same length of time in each case. The resulting mixture should be a clear solution; if turbid, more carbon tetrachloride should be added till the fat is completely dissolved. The bottle is now stoppered and allowed to stand in a dark place for the requisite time;

loss of iodine by volatilisation may be guarded against by moistening the stopper with potassium iodide solution. The time required for complete absorption varies from $\frac{1}{2}$ an hour in the case of solid fats to 2 hours in the case of drying oils.

The estimation of the excess of iodine chloride is carried out as follows: 20 c.c. of potassium iodide solution and about 300 c.c. of water are added; the mixture is then titrated with the standard sodium thiosulphate solution, shaking occasionally, in order that all the iodine may be extracted from the lower layer of carbon tetrachloride; a little starch solution is added towards the end of the titration. The difference in the number of c.c. of thiosulphate solution required in the blank test and in the actual determination is then calculated to express the percentage proportion of iodine absorbed by the fat. (The molecule of iodine chloride, ICl, is chemically equivalent to the molecule of iodine $I_2$, in the interactions involved in the process.)

The determination of the iodine value is of great importance as a method of characterising the fatty oils and fats. Owing to the comparatively low melting points of the glycerides of the unsaturated acids, there is a general tendency for oils and fats with high iodine values to possess lower melting points and a softer consistency than those with lower iodine values. This rule is, of course, sometimes modified by the nature of the saturated acid radicles, a case in point being that of cocoanut oil, which contains an unusually large proportion of saturated acid radicles of comparatively low molecular weight, and therefore possesses a rather low melting point in spite of its exceptionally low iodine value.

As was pointed out above, the drying power of oils and fats is, generally speaking, directly proportionate to the iodine value. This property of absorbing oxygen

on exposure to air at the ordinary temperature or on "blowing" with air at elevated temperatures, with the formation of more or less viscous products, finds extensive technical application. Thus linseed oil (note the high iodine value), especially after it has been treated with lead and manganese oxides at about 150°, readily dries to a tough skin when exposed to air in thin layers, and is on this account extensively used in the manufacture of paint and linoleum. Other oils, such as cotton seed and rape seed oils are often blown with air at about 150° in order to increase their viscosity for use as lubricants when mixed with mineral oils.

The diminution of the iodine values of cotton seed or rape seed oils on treatment with a current of air at about 120°, may easily be demonstrated by a small laboratory experiment.

Examples of the application of the results of iodine value determinations in the identification of the oils and fats, and the qualitative and approximate quantitative analysis of mixtures, will be found below. (See pp. 109 *et seq.*)

(*b*) *Saponification Value.*—The saponification value expresses the number of milligrams of potassium hydroxide required for the complete saponification of 1 gram of the fat. It is thus, in the case of pure fats, inversely proportional to the mean molecular weight of the acid radicles present, more alkali being required to saponify a given weight of fat consisting of acid radicles of low molecular weight combined with the glycerol residue than an equal weight of fat containing acid radicles of higher molecular weight. On this account, the saponification value affords a means of identifying or detecting certain fatty oils and fats, and at the same time, of detecting admixed unsaponifiable matter, such as paraffin, the presence of which will obviously tend to give an abnorally low value.

From the following description of the process for determining the saponification value it will be seen that some of the potash used in the determination will go to neutralise any free fatty acids which the fat may contain. If the amount of free fatty acids should be considerable

(see below, under "Acid Value"), then the saponification value found should be corrected to give the true "Ester Value" of the fat, by subtracting the weight of free fatty acids from that of the fat taken and the weight of potash required for the neutralisation of the acids from the weight of the potash used up in the determination. Similarly, in the case of notable quantities of added unsaponifiable matter being present, the weight of the latter, if estimated, may be subtracted from the weight of the sample used in the determination in order to arrive at the saponification value of the fat present in the mixture. The actual details of these calculations will be obvious from what is said below on the calculation of the saponification and acid values.

For the determination of the saponification value the following solutions will be required :—

*Alcoholic Caustic Potash Solution.*—35 to 40 grams of potassium hydroxide, purified by alcohol, are dissolved in about 40 c.c. of water, and made up to 1,000 c.c. with 96 per cent. alcohol ; the latter should be tested before use by boiling a few c.c. with an equal bulk of concentrated caustic alkali solution, whereupon only a very faint yellow coloration should be produced. The admixture of the aqueous potash and the alcohol may be facilitated by shaking and warming. After standing for a day, the clear liquor is decanted or filtered from any sediment which may have been deposited, and preserved in a bottle furnished with a well-fitting rubber stopper, so that it will be kept out of contact with atmospheric carbon dioxide. The solution should only become light yellow on prolonged standing if the alcohol used in its preparation was sufficiently pure ; otherwise it may turn dark brown.

*Standard Hydrochloric Acid of half Normal Strength.*—In the determination 1·5 to 2 grams of the fat are weighed into a 200 c.c. Jena conical flask, and 25 c.c. of the

alcoholic potash solution are added from a pipette. At the same time, a blank test is started, 25 c.c. of the same solution being measured into a similar flask, from the same pipette, in exactly the same way; this portion is to be treated in exactly the same way as the portions containing fat, in order that errors owing to absorption of carbon dioxide, and other causes, may be eliminated. The flasks are fitted with simple tube condensers, about 12 inches long, by means of rubber stoppers, and the contents are kept gently boiling on a water bath, and carefully agitated from time to time in order to hasten the saponification. This part of the process will be complete when a clear, homogeneous liquid, free from particles of fat, has been obtained, the time usually taken being from 20 minutes to half an hour; if, however, the presence of appreciable amounts of unsaponifiable matter is suspected, the boiling may be prolonged somewhat, the mixture being frequently agitated in order to prevent the occlusion of unsaponified fat. The amount of potash left over from each of the saponifications, as well as that in the blank test, is now estimated by titrating the hot solutions with semi-normal hydrochloric acid, adding 1 c.c. of a 1 per cent. alcoholic solution of phenol phthalein in each case; if the saponification products should have set to a jelly, owing to loss of alcohol, a sufficient quantity of warm alcohol, previously neutralised towards phenol phthalein, to give a clear solution, should be added.

From the difference in the titers in the blank test and in the actual test the number of milligrams of potash required to saponify 1 gram of the sample may be arrived at by a simple calculation.

Examples of the application of the results of saponification value determinations in the identification of oils and

fats, and the analysis of mixtures, will be given below. (See pp. 109 *et seq.*)

Besides furnishing a useful constant for the identification or detection of certain oils and fats, the saponification value determination often admits of the detection of unsaponifiable matter, which, if present in appreciable quantity, will be seen as an immiscible liquid or insoluble solid on diluting the neutralised saponification product with distilled water; any soap which may separate out at this stage will redissolve on warming. If it is desired to examine the unsaponifiable matter, however, the saponification must be repeated on a larger scale. (See below, under "Unsaponifiable Matter.")

(*c*) *The Reichert-Wollny Value.*—The Reichert-Wollny value expresses the number of cubic centimetres of decinormal sodium hydroxide solution required to neutralise the soluble volatile acids obtained from 5 grams of the fat by the Reichert distillation process as modified by Wollny. This method of analysis does not yield absolute results, as do the iodine and saponification value determinations, as the whole of the soluble volatile acids is not necessarily estimated, but only that portion of them which will be obtained when the process of distillation, etc., is carried out according to certain specified directions. The Reichert-Wollny process, which is described below, is essentially the same as the original Reichert-Meissl process, the only difference being the greater precision which Wollny gave to the method in prescribing the exact dimensions of the apparatus to be used and other practical details.

The first stage, consisting in the saponification of the fat, may conveniently be carried out by the method of Leffman and Beam: 5 grams of the filtered fat are placed in a flask and mixed with 20 c.c. of a glycerol-soda solution, prepared by dissolving 100 grams of pure sodium hydroxide, free from carbonate, in 100 c.c. of

water, allowing to stand till clear, and then mixing 20 c.c. thereof with 180 c.c. of pure glycerol. The mixture is heated over a naked flame with continual shaking, till it has become perfectly clear and homogeneous, the process requiring about 5 minutes. 100 c.c. of water which has been boiled for at least 10 minutes are added, and the soap is dissolved by heating. 40 c.c. of normal sulphuric acid and about 1 gram of pumice in small lumps are added, and the flask is at once con-

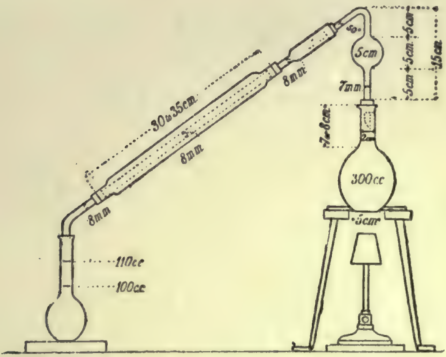


FIG. 8.—Reichert-Wollny Distillation Apparatus.

nected up to the bulb tube and condenser, for the distillation. The dimensions and form of the flask, bulb tube, condenser and receiver are shown in the accompanying illustration. The complete apparatus may be obtained from any dealer in chemical laboratory appliances. The flask, which rests on a piece of asbestos, having a circular hole in the centre, 5 cm. in diameter, is now very gently heated until the insoluble fatty acids have been completely melted, after which the heat is increased so that 110 c.c. are distilled over in the course of 30 minutes, as nearly as possible. The distillate is

shaken, filtered into a 100 c.c. measuring flask and 100 c.c. of the filtrate are titrated with decinormal baryta or soda solution, using half a c.c. of a 1 per cent. alcoholic solution of phenol phthalein as indicator. A blank test should also be made; the difference between the number of cubic centimetres of decinormal alkali used in the actual test and the blank test is the Reichert-Wollny number.

By the above process such fats as yield an exceptionally large proportion of volatile acids may be detected and approximately estimated in mixtures with other fats. The majority of fats yield Reichert-Meissl or Reichert-Wollny values below 1·0. Of the fats included in the table on p. 106, only the following three yield higher values:—

| | Reichert-Meissl Value. |
|---|---|
| Cocoanut oil .. .. .. | 7 to 8·4 |
| Palm kernel oil .. .. | 5 ,, 6·5 |
| Butter fat .. .. .. | 26 ,, 33 |

Other fats exist which give high values, but these will not be considered here. It will be noticed that Reichert-Meissl values are most frequently given in the literature; these, if carefully determined, would, however, not differ appreciably from the numbers which would be obtained by the Reichert-Wollny process.

As would be expected, the fats which yield a large proportion of volatile acids have correspondingly high saponification values, owing, of course, to the presence of large proportions of acid radicles of low molecular weight. Thus, butter fat yields notable quantities of butyric acid and the acids with even numbers of carbon atoms in the molecule, immediately following the latter, in going up the series of the fatty acids, while cocoanut and palm kernel oils are characterised by the unusually large amount of lauric acid, $C_{12}H_{24}O_2$, and myristic acid, $C_{14}H_{28}O_2$, which may be obtained from them.

The Reichert-Wollny process has been adopted as the

standard method in Great Britain for the analysis of butter and margarine.

Examples of its application will be given below.

(*d*) *Acid Value.*—The acid value is the number of milligrams of potassium hydroxide required to neutralise the free fatty acids contained in one gram of the oil or fat.

For the determination a convenient quantity, say, 25 grams of the oil or fat, are weighed off in a flask and treated with 50 c.c. of methylated spirit which has previously been neutralised with sodium hydroxide solution, using phenol phthalein as indicator. Solid fats must be melted so that they can be intimately mixed with the spirit. The mixture is kept well shaken while it is quickly titrated with decinormal sodium hydroxide solution, in presence of phenol phthalein as indicator. On standing for a short while the pink colour indicating the end point of the titration will disappear, partly owing to absorption of carbon dioxide from the air, and partly owing to the saponification of the fat; the titration should, of course, not be continued on this account. If 25 grams of fat have been used, then the number of cubic centimetres of decinormal soda used, multiplied by 0·224, gives the acid value. It is sometimes the custom to calculate the percentage of free fatty acids expressed as oleic acid; this figure may be obtained by multiplying the acid value by 0·53. If it should be necessary to correct the saponification value to give the ester value of the fat, eliminating the effect of the free fatty acids (see p. 96), then the weight of free fatty acids, expressed as oleic acid, in the sample taken for the saponification value determination may be calculated and deducted in order to find the weight of fat actually taken, and the weight of potash required to neutralise the acids present deducted from the total amount of

potash required to saponify the sample; the correction will, however, be unnecessary, unless the percentage of fatty acids be large. In the case of cocoanut oil, the free fatty acids are sometimes calculated to lauric acid, to find the percentage of which the acid value is multiplied by 0·357. The Köttstorfer value expresses the number of cubic centimetres of normal sodium hydroxide solution required to neutralise the free fatty acids in 100 grams of fat.

As mentioned above, crude vegetable oils and fats almost invariably contain appreciable quantities of free fatty acids; thus, a sample of crude cocoanut oil will probably be found to have an acid value lying somewhere between 5 and 20, while a sample of the same fat which has been refined for edible purposes will show an acid value of less than 0·3. Oils and fats which are to be used as lubricants must not contain large proportions of free fatty acids, as these would act on the bearings to form metallic soaps which would exert a clogging effect. The acid values of such oils and fats should in any case lie well under 3, while in many cases it may be well to insist on an acid value not exceeding 1.

(*e*) *Separation and Examination of the Unsaponifiable Matter.*—Under this heading will be described the method for isolating and examining the unsaponifiable matter which is a normal constituent of the fatty oils and fats. The detection and estimation of foreign unsaponifiable matter, such as paraffin wax, will be treated of later. The determination of the amount of naturally occurring unsaponifiable matter is of no importance as a method of characterising the oils and fats, owing to the varying results obtained with different samples of the same product. Further, the amount of this constituent present is usually very small, generally of the order of about 1 per cent., though in some cases, as for example in certain marine animal oils and exotic vegetable fats, it may amount to considerably more. It may also be mentioned that the waxes, which consist of esters of higher insoluble alcohols, yield from 35 to 55 per cent. of

"unsaponifiable matter," owing to the fact that these alcohols, which take the place of the soluble glycerol in the oils and fats, are obtained together with the unsaponifiable matter proper, which in this case consists mainly of higher hydrocarbons.

It has already been pointed out that the qualitative examination of the naturally occurring unsaponifiable matter of the commoner fatty oils and fats affords a valuable means of characterising the vegetable products on the one hand, and the animal products on the other; it is of especial value in the detection of the former in admixture with the latter. In what follows it is assumed that the fat is free from paraffin wax or other similar unsaponifiable matter, the presence of which would vitiate the results obtained by the operations to be described; special methods for dealing with such contingencies are, however, described in some of the works mentioned at the end of this chapter. (See "The Chemical Technology and Analysis of Oils, Fats and Waxes," by Lewkowitsch, and "Fatty Foods," by Bolton and Revis.)

The isolation of the unsaponifiable matter may be carried out as follows: 50 grams of the fat are saponified as described under the heading "Titer Test" (p. 89), using proportionate amounts of alkali, water and alcohol. The residual soap, obtained after the evaporation is complete, is dissolved in 300 c.c. of hot water and transferred to a separating funnel of about 700 c.c. capacity, using about 50 c.c. of water to rinse out the dish. After cooling, the soap solution is extracted with three successive portions of about 100 c.c. of ether. In order to avoid the formation of emulsions which only clear after prolonged standing, violent shaking should be avoided, the mixture being agitated with a rotary motion. In any case, it will probably be necessary to allow the mixture to stand overnight after the first treatment with ether; the addition of a little alcohol

may often accelerate the breaking down of an emulsion. The ethereal extracts are united and washed with water in order to remove small quantities of dissolved soap, evaporated to dryness, dried in a steam oven and, if desired, estimated by weighing.

The identification of the alcohols cholesterol and phytosterol, which in the majority of cases constitute the bulk of the unsaponifiable matter obtained from animal and vegetable fats respectively, is carried out by microscopic examination of their crystalline structure, and the determination of the melting points of their acetyl derivatives. The first mentioned method is not described here, as the indications afforded by it are less certain than those afforded by the method of determining the melting points of the acetyl derivatives, or, as it is called, the phytosteryl acetate test, the appearance of the crystals varying according to the conditions of crystallisation, especially when both alcohols are present. The method of microscopic examination which may, with practice, furnish useful indications, which may be confirmed by the phytosteryl acetate test, will be found described in some of the larger works mentioned at the end of this chapter.

*Phytosteryl Acetate Test.*—This test depends on the fact that the melting point of phytosteryl acetate lies some 10° above that of cholesteryl acetate, and that the melting point of the latter is raised by the presence of the former. It is, therefore, possible to apply the test to the detection of the adulteration of animal fats such as butter fat or lard, with vegetable fats, as, for example, cotton seed oil, cocoanut oil, etc.

The unsaponifiable matter, obtained as described above, is boiled with a small quantity of acetic anhydride in a small porcelain dish covered with a watch glass, for a minute; the excess of acetic anhydride is then evaporated off and the residue is crystallised at least three times from a few cubic centimetres of absolute alcohol,

washing the separated crops with small quantities of 95 per cent. alcohol. The melting point of cholesteryl acetate is 114·3° to 114·8°, and that of phytosteryl acetate is 125° to 130°. If only one of these substances is present either of the above melting points will readily be obtained; if both are present, the melting point of the mixture will lie somewhere between 115·4° and 125°. In dealing with the unsaponifiable matter from animal fats supposed to be adulterated with vegetable fats, it is usual to repeat the crystallisation some six or seven times; the successive crops will then contain increasing quantities of the less soluble phytosteryl acetate, if this be present, and the melting point of the material will be raised on each successive crystallisation. If, on the other hand, no phytosteryl acetate is present, the melting point will not rise above 116° C. on repeated crystallisation.

## The Identification of Fatty Oils and Fats, and the Analysis of Fatty Mixtures.

Examples of the application of the analytical methods described above, together with special tests by which certain oils and fats may be recognised or estimated, will be given under this heading. The analysis of fatty mixtures may in many cases be a matter of extreme difficulty, requiring considerable experience in this branch of analytical chemistry; the examples given below will only include comparatively simple cases of the detection of adulterations which have been known to occur in actual practice; only a limited number of the fatty oils and fats will be dealt with, while the analytical processes described in this chapter are by no means completely representative of the means available to the expert. In the table on p. 106 will be found a list of some of the more important fatty oils and fats, together with their physical and chemical constants which may be determined by methods already described.

CHEMICAL AND PHYSICAL CONSTANTS OF SOME OF THE MORE WELL-KNOWN FATTY OILS AND FATS, AND THE FATTY ACIDS DERIVED FROM THEM.

| Kind of Oil or Fat. | Specific Gravity. | Iodine Value. | | Saponification Value. | Melting Point, ° C. | Solidifying Point of Fatty Acids, ° C. | Melting Point of Fatty Acids, ° C. | Principal Uses. |
|---|---|---|---|---|---|---|---|---|
| | | Fat. | Fatty Acids. | | | | | |
| Linseed oil | At 15° C. ·9315—·9345 | 175—200 | 179—210 | 190—195 | — | 20·6 | 17·0 | Paint, varnish, linoleum, etc. |
| Cotton seed oil | At 15° C. ·922—·925 | 104—110 | 112—115 | 193—195 | — | 32—35 | 35—40 | Soap, lubricant, food. |
| Soja bean oil | At 15° C. ·924—·927 | 121—122·5 | 115·2—122 | 190·5—193 | — | 23—25 | 27—29 | Food and illuminant. |
| Maize oil (corn) | At 15·5° C. ·9213—·9255 | 119—123 | 125 | 188—193 | — | 14—16 | 18—20 | Food, soap, burning. |
| Sesame oil | At 15° C. ·9230—·9237 | 103—114 | 110—111 | 189—193 | — | 23·5 | 25—32 | Food, soap, perfumery, illuminant. |
| Rape seed oil | At 15·5° C. ·9132—·9168 | 95—100 | 99—103 | 170—179 | — | 13·6—16·0 | 20·0 | Lighting and lubricant. |
| Arachis oil | At 15° C. ·9170—·9209 | 85—100 | 96—103 | 190—196 | — | 29—30 | 30—32 | Food, soap. |
| Olive oil | At 15° C. ·916—·918 | 80—86 | 86—90 | 185—196 | — | 17—26 | 26—28 | Food, soap, wool treatment, illuminant, etc. |
| Castor oil | At 15·5° C. ·960—·968 | 85—95 | 87—93 | 183—186 | — | 3·0 | 13·0 | Medicine, soap, lubricant. |
| Menhaden oil | At 15·5° C. ·927—·933 | 139—173 | — | 189—192 | — | — | 21—25 | Burning, lubricant. |
| Seal oil | At 15° C. ·9155—·9263 | 130—152 | — | 190—193 | — | 15·9 | 22—23 | Illuminant, lubricant, currying leather, etc. |
| Whale oil | At 15° C. ·917—·929 | 110—146 | 130—132 | 188—194 | — | 22·9—23·9 | 14—27 | Leather-dressing, burning, soap. |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Cod-liver oil (medicinal). | At 15° C. ·921—·927 | 130—181·3 | 130·5—170 | 175—185 | — | — | 50—52 | Medicine, currying leather, etc. |
| Neat's foot oil | At 15° C. ·914—·916 | 69·3—76 | — | 194·3—199 | — | 26·5 | — | Lubricant for fine machinery, wool treatment. |
| Cacao butter | At 98° C. ($H_2O$ at 15·5° C. = 1) ·8577 | 32—41 | 33—39 | 194—197 | 32—33 | 46—49 | 49—50 | Chocolate, confectionery, pharmacy, perfumery. |
| Palm oil | At 98 — 99° C. ($H_2O$ at 15·5° C. = 1) ·8586 | 51·5—57 | 53·3 | 196—205 | 36—37 | 36—45·5 | 47—48 | Soap and candles, etc. |
| Palm kernel oil | At 99° C. ($H_2O$ at 15·5° C. = 1) ·8731 | 13—17 | 12·0 | 242—250 | 26—29 | 20—22 | 20·7 | Soap, food, etc. |
| Cocoa nut oil | At 100° C.—99° C. ($H_2O$ at 15·5° C. = 1) ·874—·904 | 8—10 | 8·4—9·3 | 246—260 | 23—25·5 | 22—25 | 24—25 | Soap, food, etc. |
| Butter fat | At 100° C. ($H_2O$ at 15° C. = 1) ·865—·904 | 26—50 | 28—33 | 220—233 | 28—33 | 33—35 | 38—40 | Food. |
| Beef tallow | At 98° C. ($H_2O$ at 15·5° C. = 1) ·8626 | 36—48 | 41·3 | 193—200 | 43—49 | 43—45 | 43—47 | Food, soap, candles, etc. |
| Mutton tallow | At 100° C. ($H_2O$ at 15·5° C. = 1) ·858—·860 | 35—44 | 34·8 | 192—195 | 35—48 | 41—46 | 46—48 | Food, candles, soap. |
| Lard. | At 100° C. ($H_2O$ at 15·5° C. = 1) ·8589—·8641 | 49—70 | 64—81 | 195—197 | 32—48 | 34—39 | 37—38 | Food, candles, soap, lubricant. |
| Lard oil | At 15° C. ·916 | 67—88 | — | 193 | — | — | — | Food, soap, wool treatment, lubricant. |

The above figures are based on values quoted by Lewkowitsch and others.

In the first place, the determination of the acid value and the saponification value or the unsaponifiable matter will show how far the sample consists of neutral glycerides. The specific gravity, which will generally only be determined in the case of the liquid oils, will not afford much definite information ; in some cases abnormal values may give useful indications of adulterants to be looked for, or confirmation of conclusions arrived at by other means. The determination of the iodine value, on the other hand, is of great use in the analysis of mixtures, owing to the considerable variations in this constant with the different oils and fats. As regards the saponification value, it will be noticed that the majority of the oils and fats have values lying in the neighbourhood of 190 ; rape, castor, and cod liver oils will be seen to be characterised by lower, and butter fat and cocoanut and palm kernel oils by higher, values. For reasons already pointed out, samples having high saponification values should be examined by the Reichert-Wollny process for volatile acids. The limitations of the use of the determination of the melting points of oils and fats for their identification, has already been pointed out. Regarding the methods for examining the insoluble fatty acids, the titer test may often be of great value, while the determination of the iodine values of the fatty acids may be resorted to when the original sample contains large quantities of added unsaponifiable matter from which it cannot be separated.

In addition to the chemical and physical methods, the taste and smell, especially on warming, of the sample, may afford useful indications. Even the non-expert may in some cases be guided by these methods, as for example, in the detection of fish oils, especially if comparison be made with genuine samples. Matters may sometimes be simplified for the analyst by considerations of relative cost ; thus if a sample purporting to consist of a certain kind of oil or fat appears not to be genuine, it is obvious that the adulterant or substitute will only consist of a material which is cheaper at the ruling market prices.

*The Detection and Estimation of Adulterants in Olive*

*Oil.*—Of the possible adulterants of olive oil, the following will be considered: cotton seed oil, sesame oil, lard oil, arachis oil and rape seed oil.

*Ex.* I. *Cotton Seed Oil in Olive Oil.*—On reference to the list of iodine values in the table, it will be noticed that olive oil possesses a lower iodine value than any of the adulterants named above, with the exception of lard oil. Although, in exceptional cases, perfectly genuine samples of olive oil have been known to give iodine values above 90, yet a sample showing an iodine value above the limits given in the table should be regarded with suspicion.

Cotton seed oil may be detected in presence of other oils by the Halphen test, which is carried out as follows: About 2 c.c. of the sample are mixed with an equal volume of amyl alcohol in a test tube, and about 2 c.c. of a 1 per cent. solution of sulphur in carbon disulphide are added. The tube is then placed in a beaker of warm water which is gradually heated to boiling. In the presence of cotton seed oil, a characteristic orange red coloration will be developed after heating in the boiling water for about 10 minutes. It should be noted that cotton seed oil which has been heated above 200° C. does not respond to the Halphen test.

E. Gastaldi (see *Journ. Chem. Soc.*, Abstracts ii., 1912, p. 1108) has found that cotton seed oil does not respond to the Halphen test when this is carried out with carefully purified amyl alcohol, in vessels free from all traces of alkali. Concluding that the reaction depends on the presence of traces of basic substances, this author has modified the Halphen test as follows: 2 c.c. of the oil are treated with 1 drop of pyridine and about 4 c.c. of a 1 per cent. solution of sulphur in carbon disulphide, and the mixture is heated in the water bath.

This test is more delicate than the original Halphen test, and can be recommended in its place. It is, however, subject to the same limitations as the latter. (See above.)

Other colour reactions for cotton seed oil are known, but these are, generally speaking, not so reliable as the Halphen test.

If a positive reaction for cotton seed oil has been obtained, the extent of the adulteration may be approximately calculated from the iodine value of the sample as follows: Supposing the iodine value found to be 93. Then, taking the average iodine values of cotton seed and olive oils as 106 and 83 respectively, let $x$ equal the percentage of cotton seed oil in the sample.

$$\text{Then } \frac{100 - x}{100} 83 + \frac{106}{100} x = 93.$$

Whence $x =$ from 40 to 45 per cent.

It will be observed that the difference between the saponification values of the two oils is not sufficiently great to afford a means for detecting the adulterant; this would also be the case if any of the possible adulterants mentioned above, with the exception of rape oil, were present. Confirmation of the presence of cotton seed oil might possibly be obtained from a somewhat high specific gravity and titer test, or melting point of the fatty acids, though the latter figures would not afford any basis for quantitative calculations.

*Ex. 2. Sesame Oil in Olive Oil.*—If the sample shows a higher iodine value than would be expected from genuine olive oil, and gives a negative test for cotton seed oil, then sesame oil should be tested for by the Baudouin test as follows: 10 c.c. of the oil are treated with 10 c.c. of concentrated hydrochloric acid and 2 drops of a 2 per cent. solution of furfuraldehyde; the mixture

is shaken vigorously for one minute, and then allowed to stand to separate; in the presence of sesame oil the aqueous layer will be coloured a strong crimson.

This reaction allows of the detection of small quantities of sesame oil in mixtures, and is one of the most reliable of the colour reactions applied to oils and fats. For these reasons, the addition of sesame oil to margarine has been made compulsory in Germany and other countries, in order to provide a ready means of recognising this article of food. As the colouring matters in margarine or butter sometimes produce a red coloration with concentrated hydrochloric acid, it is necessary, when testing for sesame oil in these, to wash the sample two or three times with the concentrated acid before applying the actual test.

The proportion of sesame oil present in olive oil may be roughly calculated from the iodine value of the sample and the iodine values of sesame and olive oils, as shown in Ex. 1.

*Ex.* 3. *Lard Oil in Olive Oil.*—In this case the adulteration would not be revealed by the saponification value, while the iodine value would only be slightly lowered. The odour of lard oil would, however, be noticeable on warming, and its presence could be confirmed by the phytosteryl acetate test (p. 104).

*Ex.* 4. *Arachis Oil in Olive Oil.*—If the sample shows a somewhat high iodine value and gives negative Halphen and Baudouin tests, arachis oil should be tested for by Bellier's test, and if found to be present, estimated by Renard's method as modified by Archbutt. Both of these tests, which are described below, are applicable to mixtures of liquid vegetable oils and cocoanut and palm kernel oils, but break down in the presence of other solid fats, vegetable or animal.

*Bellier's Test for Arachis Oil.*—Before proceeding with the actual test the following two solutions must be prepared :—

Alcoholic potassium hydroxide solution, made by dissolving 4·25 grams of stick potash, pure by alcohol, in 70 per cent. alcohol, and making up to 50 c.c.

Acetic acid solution of such a strength that 1·5 c.c. will neutralise exactly 5 c.c. of the potash solution.

To carry out the test, 1 gram of the oil is placed in a boiling tube 6 in. long and 1 in. in diameter, and saponified by gently heating with 5 c.c. of the alcoholic potash solution, shaking well and moderating the heating so as to avoid loss of alcohol by evaporation. When a homogeneous clear solution has been obtained, 1·5 c.c. of the acetic acid are added, and the tube is cooled in water at 18° for at least half an hour, with occasional shaking. 50 c.c. of 70 per cent alcohol, containing 1 c.c. of concentrated hydrochloric acid per 100 c.c. are added, and the mixture is kept in water at 18° for an hour.

If 5 per cent. or more of arachis oil was present in the original sample, a precipitate, consisting chiefly of arachidic acid (see pp. 79, 114), will be formed, but if no arachis oil was present, the solution will remain clear or, at the most, become slightly turbid. The presence of solid animal or vegetable fats, other than cocoanut or palm kernel oils, will give rise to the formation of a precipitate which would mask the test for arachis oil.

*Determination of Arachis Oil as Arachidic Acid.* (*Renard's Method modified by Archbutt.*)—The determination is based on the fact that, while arachis oil yields some 4 to $5\frac{1}{2}$ per cent. of acids of melting point 74° to 75·5° C., consisting mainly of a mixture of arachidic acid, $C_{20}H_{40}O_2$, and lignoceric acid, $C_{24}H_{48}O_2$, olive and most other oils yield, at the most, only traces of these

acids. In isolating the crude arachidic acid advantage is taken of the solubility of the lead salts of the unsaturated fatty acids, *e.g.*, oleic acid, in ether, and the insolubility of the lead salts of the alphatic acids such as stearic and arachidic acids in this solvent. Having removed the unsaturated acids, the arachidic and lignoceric acids are separated from the more soluble aliphatic acids of lower molecular weight by crystallisation from alcohol.

For the determination, 10 grams of the oil are saponified by alcoholic potash, and the soap which remains after removal of the alcohol by evaporation is dissolved in water. The soap solution is acidified with dilute hydrochloric acid and the free fatty acids are extracted with ether. The ether is evaporated off and the acids are dissolved in 50 c.c. of 90 per cent. alcohol by heating, and, without allowing the solution to cool so as to deposit crystals, 5 c.c. of a 20 per cent. solution of lead acetate are added. It will be noticed that the amount of lead acetate added is insufficient to precipitate the whole of the fatty acids present as lead salts; the whole of the arachidic and lignoceric acids will, however, according to Archbutt, be contained in the precipitate; by using this method of fractional precipitation, the subsequent process of dissolving out the lead oleate, etc., is considerably shortened. The mixture is cooled to 15°, agitated and allowed to stand for half an hour, after which the precipitate is filtered off and washed once with ether. The lead salts are then washed back into the flask by means of ether, and digested with the latter on the water bath, brought back on to the filter, the whole process being repeated twice. The lead salts are transferred to a separating funnel by washing with ether, decomposed by dilute hydrochloric acid, and the ethereal layer, con-

taining the liberated acids in solution, is washed with water till free from mineral acid. The ethereal solution is transferred to a flask, evaporated to dryness, and the solid acids thus obtained dried at 100°.

50 c.c. of 90 per cent. alcohol are added to the acids in the flask, which is then corked lightly and warmed until the acids are dissolved ; the solution is cooled to either 15° or 20°, kept at this temperature for 3 hours, after which the crop of crystals is filtered off on a Gooch crucible and washed with 3 portions of 10 c.c. of 90 per cent. alcohol at the same temperature. The filtrate and washings of 90 per cent. alcohol from this and subsequent operations should be measured, in order that a correction for the dissolved arachidic acid may be introduced. The washing should not be carried out too rapidly, as the alcohol passing through the filter should become saturated with the acid. The crystals are then washed with 70 per cent. alcohol ; these washings may be rejected, as practically no arachidic acid will be dissolved. The crystals are dissolved from the filter by warm ether, which is evaporated in a tared flask, and the residue dried and weighed. The melting point of the acids is determined in the usual way ; if this is found to be under 71° the process of recrystallisation and washing must be repeated as described above, the quantity of 90 per cent. alcohol used being noted as before.

The amount of arachidic acid estimated to have been dissolved by the 90 per cent. alcohol is added to that actually weighed. The amount of arachis oil in the original sample may then be approximately calculated by multiplying the total arachidic acid by 20, as it has been found that arachis oil yields about 5 per cent. of arachidic acid melting at 71 to 72·5 by the method described.

In order to allow for the dissolved acid the following table, due to Archbutt (abridged), may be used :—

| Weight of Acids obtained. (grams) | Grams of Acids dissolved by 100 c.c. of 90°/₀ Alcohol at | | |
|---|---|---|---|
| | 15° C. | 17·5° C. | 20° C. |
| 0·1 or less . | 0·033 | 0·039 | 0·046 |
| 0·3 . . | 0·055 | 0·064 | 0·074 |
| 0·5 . . | 0·064 | 0·075 | 0·085 |
| 0·8 or more. | 0·070 | 0·080 | 0·091 |

In the presence of solid animal and vegetable fats, the test is not so satisfactory in its quantitative application, but may still be used qualitatively in cases where Bellier's test breaks down ; according to Lewkowitsch, it is possible to estimate approximately arachis oil in lard by Renard's test. In such cases, however, it may be necessary to recrystallise repeatedly from 90 per cent. alcohol before an arachidic acid melting over 70° is obtained, while a negative result cannot always be taken as evidence of the absence of arachis oil.

Arachis oil is very frequently used as an adulterant in olive oil; as will be seen from the table on p. 106, the saponification value or specific gravity of the sample would not reveal the presence of this adulterant, while the difference between the iodine values of olive and arachis oils is not very great.

*Ex.* 5. *Rape Oil in Olive or Arachis Oils.*—The presence of considerable quantities of rape oil in olive oil might be indicated by a somewhat high iodine value, but

in the case of arachis oil supposed to be adulterated with rape oil, no definite information could be obtained from the result of the determination of this constant. Bearing in mind the comparatively low saponification value of rape oil, it is evident that samples of olive or arachis oils adulterated with appreciable quantities of rape oil should show abnormally low saponification values. In this connection it may be mentioned that of the oils and fats given in the table on p. 106, which have low saponification values, rape oil is the only one which would be likely to occur as an adulterant of arachis or olive oils.

The approximate proportion of rape oil present might be calculated from the saponification value of the sample as follows: Supposing that a suspected sample of arachis oil was found to have an iodine value of 97, and a saponification value of 187. Then, taking the mean saponification value of arachis oil as 193·5, and that of rape oil as 174·5, if $x$ equals the percentage of rape oil present,

$$\frac{100 - x}{100} 193 + \frac{174{\cdot}5\,x}{100} = 187,$$

whence $x =$ from 30 to 35 per cent.

In this case the determination of the specific gravity would be of little use, but a sample of arachis oil adulterated with rape oil might show an abnormally low titer test.

As rape oil has been shown to contain only very small amounts of arachidic acid, a determination of arachis oil as arachidic acid could be made as described above, in order to check the result obtained from the calculation based on the saponification value.

*Ex.* 6. *Cotton Seed Oil in Rape Seed Oil.*—The presence of cotton seed oil as an adulterant in rape seed oil would be revealed by a higher saponification value than would

be expected from pure rape oil, and might be confirmed by the Halphen test for cotton seed oil. The iodine value, titer test, and specific gravity would all tend to be raised owing to the presence of the adulterant, though these figures, excepting, perhaps, the titer test, would not be noticeably influenced unless the amount of cotton seed oil present was large. The extent of the adulteration might be approximately calculated from the saponification value of the sample and the mean saponification values of cotton and rape oils, as described above in Ex. 6.

*Ex.* 7. *Arachis Oil, Sesame Oil, or Cotton Seed Oil in Lard.*—The presence of any of these oils might be indicated by a high iodine value. Sesame and cotton seed oils could be detected by the Baudouin and Halphen tests respectively (see Exs. 1 and 2), and their presence could be confirmed by the phytosteryl acetate test for detecting vegetable oils and fats. Confirmation by this means should always be sought if cotton seed oil is suspected to be present, as it has been shown that lard from pigs which have been fed on cotton seed cakes may itself give a positive Halphen test. If negative Baudouin and Halphen tests have been obtained, arachis oil should be tested for and estimated, if present, by the method detailed in Ex. 4. Here, again, the phytosteryl acetate test might be applied to confirm the presence or absence of a vegetable oil.

*Ex.* 8. *Arachis, Sesame, or Cotton Seed Oils in Cacao Butter.*—The adulteration of cacao butter, or chocolate fat, with the above mentioned oils could be detected on the same lines as indicated in the previous example, excepting, of course, that the phytosteryl acetate test would in this case not be available, as cacao butter is itself a vegetable product. As cacao butter has a fairly

low iodine value, the extent of the adulteration might be approximately calculated as indicated in Ex. 1. The titer test and melting point of the fatty acids of cacao butter are fairly high, and would tend to be lowered through the presence of the oils in question. A determination of the melting point of the sample should also be made, as it is important that fats used in chocolate making should not melt at too low a temperature.

*Ex.* 9. *Cocoanut or Palm Kernel Oils in Lard or Cacao Butter.*—These adulterants, if present in appreciable quantity, would be indicated by a low iodine value and high saponification value. A fairly high Reichert-Wollny value would afford confirmation of their presence. Thus, lard and cacao butter give values of about 0·5 and 0·75, respectively; from the figures given under the description of the method for carrying out the Reichert-Wollny determination, it might be concluded, for example, that a sample of lard showing a Reichert-Wollny value of about 1·5 would contain about 10 per cent. of cocoanut oil, or rather less palm kernel oil. The phytosteryl acetate test would only be available in the case of lard. The titer test, or melting point of the fatty acids, would tend to be lowered through the presence of the adulterants under consideration.

*Ex.* 10. *Fish or Blubber Oils in Rape Oil.*—Fish or blubber oils may often be detected in mixtures by their characteristic smell which becomes more noticeable on warming. The presence of these adulterants would tend to raise both the saponification and the iodine values, especially the latter. Fish or marine animal oils, and other drying oils such as linseed oil, may be distinguished from, and detected in the presence of non-drying and semi-drying oils such as rape oil, cotton seed oil, arachis oil, etc., by means of the Hexabromide test, which

is based on the fact that the hexabromo (or octobromo) derivatives yielded by the first mentioned group are practically insoluble in ether and certain other solvents; the semi and non-drying oils, on the other hand, are only capable of yielding lower bromine addition products which are soluble under the conditions of the test. (See p. 79.)

Halphen's modification of the hexabromide test is as follows: 0·5 c.c. of the oil are mixed with 10 c.c. of a mixture of 28 parts by volume of glacial acetic acid, 1 part of bromine and 4 parts of nitrobenzene, in a clean, dry test tube, the tube is closed and shaken, and the contents examined. The semi- or non-drying oils produce, at the most, only a slight turbidity, while the fish or marine animal oils, or other drying oils, produce a distinct precipitate which is not dissolved on the addition of 10 c.c. of methylated ether. Rape oil gives a turbid liquid separating into two layers, but on the addition of 10 c.c. of ether, a clear liquid is formed.

The indications afforded are, of course, only of a qualitative nature, but the test would prove useful in deciding whether a sample of rape oil, showing an abnormally high iodine value, had been adulterated with a fish or other drying oil, or with larger quantities of a semi-drying oil having an iodine value higher than rape oil. Bolton and Revis state that as little as 5 per cent. of fish, marine animal or drying oil may be detected in rape oil, but that the test breaks down in the presence of animal fats such as beef tallow and lard, which produce a precipitate under the conditions of the test. Shea butter is stated to behave similarly to the animal fats.

*Butter Adulterated with Margarine.*—The detection of margarine fats in butter fat may often be a far more

complex problem than any of those hitherto considered, owing, firstly, to the fact that the margarine fat will practically always be a mixture, and, secondly, to the fact that the chemical and physical constants of genuine butter fats may vary within fairly wide limits, depending on factors such as the breed and age of the cow, nature of the fodder, climatic conditions and general treatment of the animals.

Margarine usually differs from butter in the composition of the fat only; the fats commonly used in margarine making are cocoanut and palm kernel oils, beef tallow and lard, in addition to which oils such as cotton seed, arachis and sesame oils are practically always present. The detection of quantities up to about 10 per cent. of margarine fat in butter fat may often be a matter of considerable difficulty, especially as some of the constants of the added fat mixture may approximate closely to those of pure butter fat. For example, the tendency for the iodine value to be lowered, owing to the presence of cocoanut or palm kernel oils, might be neutralised by the presence of another oil with an iodine value higher than that of butter fat.

The most important method for the examination of butter fat is the Reichert-Meissl or Reichert-Wollny process for estimating the volatile acids yielded by the fat, the latter having been adopted as the standard method for the examination of butter fat in Great Britain. The majority of butter fats yield Reichert-Wollny values lying between 26 and 33, while none of the fats which can be used as adulterants yield higher values. A butter fat showing a Reichert-Wollny value of 24 to 25, or less, should, therefore, be regarded with suspicion, though it could not be definitely said to be adulterated unless the Reichert-Wollny value were below 20, as

exceptional examples have been known of perfectly genuine butter fats yielding values approximating to this figure. In doubtful cases, recourse should be had to the phytosteryl acetate test for the detection of vegetable oils and fats. At the same time the colour tests for sesame and cotton seed oils might be applied (see Exs. 1 and 2). As cocoanut and palm kernel oils yield moderately high Reichert-Wollny values (see p. 100), their presence would not have so marked an effect as the presence of other vegetable oils or animal fats; on the other hand, being vegetable products, they would be revealed by the phytosteryl acetate test. The presence of cocoanut or palm kernel oils only would tend to lower the iodine value and raise the saponification value, while the Reichert-Wollny value might not be greatly affected. If the other vegetable oils mentioned above were present as well, the iodine and saponification values might not be affected to any noticeable extent. Adulteration with animal fats together with vegetable oils other than cocoanut and palm kernel oils, would produce a greater effect on the Reichert-Wollny value than in the case just considered, while the iodine value would probably be raised, and the saponification value lowered.

The above methods will suffice, at least, to distinguish between genuine butter and margarine or butter containing, say, 25 per cent. or more of margarine. Smaller amounts of added fats may, in some cases, also be detected, but may, on the other hand, be overlooked unless the sample is subjected to a still more searching examination. This is especially the case if the added fat consists of cocoanut oil, for the detection of which, numerous special methods have been proposed. The most well-known of these is Polenske's modification of the Reichert distillation process, in which the water

soluble and insoluble volatile fatty acids are separately estimated. Blichfeldt (*Journ. Soc. Chem. Ind.* No. 13, Vol. XXIX.) has designed a special distillation apparatus in which the side tube, condenser and receiver are all in one piece, and estimates the volatile fatty acids forming water soluble and insoluble silver salts; this method admits of a sharper differentiation between cocoanut and palm kernel oils and butter fat than the methods hitherto mentioned. Other methods for the examination of butter fat are the determination of the refractive index and the microscopic examination of the crystalline structure of the fat. Descriptions of these methods, as well as the Polenske method, will be found in the works of reference enumerated at the end of this chapter.

*The Detection of Paraffin Wax in Lard or Cacao Butter.*—The following method was devised by Polenske for the detection and estimation of paraffin wax in lard. It may also be applied to the detection of this adulterant in other fats.

100 grams of the sample are saponified by boiling in a flask connected with a reflux condenser, with alcoholic potash in the proportions recommended above under the directions for the isolation of fatty acids from fats (p. 89). The paraffin wax, if present, will be noticed as a layer floating on the soap solution. The process of saponification should be complete after an hour's boiling, the mixture being well shaken from time to time. If the amount of paraffin wax present is large, it may be necessary to prolong the treatment in order to secure complete saponification of the fat. After removal of the alcohol by evaporation, the unsaponifiable matter, including the paraffin wax, is separated as directed on p. 103. In order to eliminate the naturally occurring unsaponifiable matter, and to separate the paraffin wax

for estimation and examination, the total unsaponifiable matter is heated in a test tube immersed in a brine bath at 105° C., with 5 c.c. of concentrated sulphuric acid for half an hour. After cooling, the mixture is extracted without previous dilution, with petroleum ether which is completely volatile below 80°. The extraction having been repeated twice with fresh quantities of petroleum ether, the petroleum ether extracts are united and evaporated to dryness in a tared flask. The residue, consisting of paraffin wax, is dried at 100° and weighed.

From the above examples it may be seen how the analytical processes described in this chapter may be applied in the analysis of simple mixtures of the more well-known fatty oils and fats, or identifying unadulterated samples of the latter. The examples of adulteration given are all comparatively simple; in actual practice, however, problems may occur which will require for their solution more extensive investigations and greater experience in this branch of analytical chemistry than can be obtained from the present work. The student wishing to pursue the subject further is recommended to consult the works mentioned below, especially Lewkowitsch's "Chemical Technology and Analysis of Oils, Fats and Waxes."

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# CHAPTER IV

## SOAP

### Introductory.

Soap consists essentially of the sodium or potassium salts of the fatty or rosin acids, and is produced by the action of caustic alkali on fats, fatty acids or rosin. All soaps contain notable quantities of water, the proportion of which may vary within wide limits, while the potash or soft soaps and some soda soaps such as the marine soaps, contain, in addition, the glycerol which is produced in the process of saponifying the fat. Other possible constituents of soaps are mentioned in the classification given below.

Soap is generally manufactured by treating fat with a definite proportion of caustic alkali solution, the saponification being effected either by boiling the mixture in open vessels, heating under steam pressure in closed vessels, or, as in the cold process, by allowing the soda solution to act on the fat (usually cocoanut oil) at the ordinary or slightly elevated temperatures. The soda soaps produced according to the two first mentioned methods are separated from the excess of water and alkali, and the glycerol, by adding a solution of common salt to the boiling mixture; the sodium salts of the fatty acids, being insoluble in sodium chloride solution, separate out, together with a relatively small proportion of water, as a molten layer on the surface of the brine which retains the greater part of the glycerol and excess of free alkali. Soaps made by the cold process, as well as the potash or soft soaps, are not submitted to this process of purification and, therefore, contain glycerol, excess of free alkali and a large proportion of water.

The rosin, or colophony, which is used in conjunction with fats in the manufacture of cheaper soaps, consists

of the residue which remains after distilling off the oil of turpentine and moisture from pine resin; it is chiefly composed of acids which dissolve in caustic alkali solution with the formation of soap-like products which generally differ from the true soaps produced from fats in possessing greater alkalinity, and being softer and darker in colour. Rosin or colophony should be distinguished from the rosin spirit or rosin oils which are produced from it by destructive distillation. (See Chapter V., p. 179.)

The fats most commonly used in soap making are tallow, palm oil, recovered grease, cocoanut oil, cotton seed oil, maize oil, sesame oil, hemp seed oil, palm kernel oil, various fish oils, castor oil, olive oil and lard. In the case of edible fats, it is usually the cheaper grades which are used in soap making.

The cleansing action of soap depends, firstly, on the formation of small quantities of free caustic alkali owing to the hydrolytic action of water on the alkali salts of the fatty or rosin acids; according to the principles of mass action, the greater the proportion of water to soap, the greater will be the extent of the hydrolysis, so that the concentration of free caustic alkali is to some extent automatically regulated and kept low; further, the greater causticity of rosin soaps as compared with soaps formed from fats, may be explained by the fact that the rosin acids are weaker acids than the fatty acids, and, consequently, their sodium salts are hydrolysed to a greater extent in aqueous solution. The removal of dirt of a greasy nature, which cannot be effected by means of water alone, takes place as follows: a small portion of the fatty matter is saponified by the caustic alkali and removed as soluble soap; the greater portion, however, is made into an emulsion with the alkaline liquid and mechanically removed with the lather.

The various soaps on the market may be broadly classified as follows:—

(1) *Toilet Soaps*.—These should consist as far as possible of the neutral sodium salts of the fatty acids together with moderate amounts of water. They should, naturally, contain no impurities or adulterants, and,

above all, no free caustic alkali or alkaline carbonate. They are often made from lard or olive oil. The transparent toilet soaps which are produced by dissolving soap in alcohol and evaporating the clear solution, generally contain glycerol, and sometimes also notable amounts of sugar.

(2) *Laundry Soaps.*—These usually contain more or less free alkali as carbonate or hydroxide. They are usually made from tallow, palm oil or rosin.

(3) *Commercial Soaps.*—The soft soaps, which are generally made from fish oils or vegetable drying oils, contain glycerol and excess of potash and water. The so-called hydrated soaps, which are produced from cocoanut or palm kernel oils by the cold saponification process, contain glycerol and excess of water; they are also liable to contain unsaponified fat and free alkali, owing to the incompleteness of the saponification process. Marine soaps are made from cocoanut or palm kernel oils; they contain a large proportion of sodium laurate, $C_{12}H_{23}O_2Na$, and sodium myristate, $C_{14}H_{27}O_2Na$, which are more soluble in salt water than the soaps from other fats, and may, therefore, be used with sea water.

(4) *Medicated Soaps.*—These may contain phenol, cresols, naphthalene, and other coal tar products, or substances of a similar nature.

Besides unsaponified fat, free alkali, or free fatty acids, soaps may contain small amounts of chlorides, sulphates, silicates and other inorganic impurities derived from the materials used in their manufacture. According to Allen, the following additions are sometimes made to soap: oatmeal, bran, sawdust, fuller's earth, chalk, etc. Considerable quantities of sand or powdered quartz are used in scouring soaps. Sodium or potassium carbonates are added to scouring and commercial soaps in order to increase their detergent properties and also to facilitate lathering with hard waters. Iron compounds, ochre, ultramarine and other colouring matters are added to produce the effect of mottling. Sodium silicate, aluminate and borate, petroleum and naphtha may also be found in commercial soaps.

## The Analysis of Soap.

Among the more important constituents to be determined, are water, total alkali, fatty and rosin acids, free alkali as carbonate and hydroxide, and combined alkali present as soap. The estimation of adulterants, or fillers and legitimate additions such as alkaline carbonate silicate and phenol, will also be described. The following scheme for the analysis of soap, which will first be briefly summarised here, is, in the main, identical with that due to Allen, Leeds, and others, which is adopted in Allen's "Commercial Organic Analysis," 1911 edition.

*Scheme of Analysis*.—The sample for analysis should, in the case of a solid soap, be taken from the interior of the bar or cake, avoiding the outer dried portions. It should be weighed between watch glasses in order to prevent loss of moisture during weighing. Water is estimated, as described under (*a*), by heating the sample and determining the loss in weight. For the estimation of unsaponified fat and other matter soluble in petroleum ether, such as petroleum or coal tar products, the dried sample, as obtained from the above operation, is extracted with petroleum ether, as described under (*b*). For the estimation of the total fatty or rosin acids, the material from the previous operation is exhausted with hot water, and the liquid filtered ; the filtrate containing in solution the soap and free alkali is treated with a known volume of normal nitric acid, slightly in excess of that required to precipitate the whole of the fatty or rosin acids ; the latter are separated and estimated, as described under (*c*), and further examined, as described under (*l*) and (*m*).

If, as is often the case, the amount of petroleum ether soluble material is small, the extraction with petroleum ether may be omitted, and operation (*c*) may be commenced, either with the dried material from the water determination, or with a fresh quantity of the soap.

The aqueous solution is filtered, if necessary, prior to the acidification with nitric acid.

The liquid from which the fatty or rosin acids have been precipitated and removed is now titrated with standard potassium or sodium hydroxide solution, using methyl orange as indicator; from the number of cubic centimetres of alkali solution required to produce neutrality, and the amount of normal nitric acid previously added, the total alkali of the soap may be calculated; this operation is described under (*d*). The neutralised liquid thus obtained is made up to a definite volume and divided into five aliquot portions in which the following constituents may be determined as described under the respective headings: soluble fatty acids (from cocoanut or palm kernel oils) (*e*), chlorides and sulphates (*f*), glycerol (*g*), sugar and glycerol (*h*).

For the estimation of the remaining constituents a fresh sample is taken and extracted with absolute alcohol; the filtered alcohol will contain in solution the soap proper, and any free caustic alkali which may have been present, while the alkali carbonate or silicate, sand, sawdust, chalk, etc., will remain on the filter. This operation, including the estimation of the free caustic alkali in the alcoholic solution by titration, is described under (*i*). The residue on the filter is exhausted with water, and the alkali carbonate, silicate, borate or aluminate, determined in the solution as described under (*j*). The insoluble residue is examined as described under (*k*).

The various operations which have been outlined above are described in detail below. Subsequently, the estimation of phenols and neutral hydrocarbons in soap will be described, and finally the analysis of phenolic disinfectants containing soap, such as lysol and creoline, will be dealt with.

(*a*) *Water.*—The following method is due to Watson Smith: 5 to 10 grams of the soap, reduced to fine shavings, are placed in a large porcelain crucible which is set in a sand bath, heated by a small Bunsen flame. The soap is continually stirred with a glass rod (weighed with the crucible) having a rough jagged end to facilitate the breaking up of the mass. The process is usually complete in 20 to 30 minutes; when, on removing the flame, a piece of plate glass placed over the dish no longer collects moisture, the heating may be discontinued, and the dish and contents, together with the glass rod, allowed to cool and weighed. The loss in weight represents water with possible traces of alcohol and essential oils. Burning of the soap must, of course, be avoided; this will, however, if it occurs, immediately be noticed by the characteristic odour produced. The results of this process are stated to be accurate to within 0·25 per cent., which is sufficient for technical purposes.

As will be seen from the table of typical analyses of soap on p. 147, the percentage of water varies very considerably in the different grades of soap. The best toilet soaps may contain as little as 10 to 13 per cent. of water, while some of the inferior hydrated varieties will contain as much as 70 to 80 per cent. Soft soap usually contains about 35 to 45 per cent. of water, and a good yellow soap some 15 to 25 per cent.

(*b*) *Unsaponified Fat and other Matter Soluble in Petroleum Ether.*—A weighed quantity of the soap, dried as described above, is placed in an extraction thimble of fat-free filter paper, and exhausted with petroleum ether which is completely volatile below 80°, in a Soxhlet apparatus. (See p. 66.) The petroleum ether extract is evaporated to dryness in a tared flask, dried at 100° and weighed. In addition to extraneous unsaponifiable matter, such as vaseline, coal tar pro-

ducts, etc., the residue thus obtained will contain any unsaponified fat or free fatty acids which may be present, together with traces of essential oils added as perfumes, and unsaponifiable matter occurring naturally in the fats. Unless, however, notable amounts of foreign material have been added to the soap, this residue should, in most cases, be very small. The estimation of phenols and neutral oils in soap is described in a subsequent portion of this chapter. In Allen's "Commercial Organic Analysis," 1911 edition, Vol. II., p. 425, will be found a systematic scheme for the examination of the petroleum ether soluble material from soap.

(*c*) *Fatty and Rosin Acids.*—As pointed out above, if the soap does not contain any appreciable amount of petroleum ether soluble material, and the last operation has been omitted, the operation now to be described may be commenced, either with a fresh portion of the original sample or the residue from the water determination. The material, if previously treated with petroleum ether, is spread out and warmed gently so that the solvent may evaporate; it is exhausted with boiling water, and the aqueous solution filtered or decanted from any insoluble matter that may be present. Normal nitric acid is then added from a burette until no further precipitate is formed; about 10 to 20 c.c. of the acid are further added, and the total quantity used is noted. The precipitated acids are allowed to solidify, and the aqueous liquid is decanted off and preserved for further examination. The acids are re-melted and mixed with hot water, allowed to solidify and the water decanted off and added to the main portion; this process is repeated two or three times, after which the acids are filtered off and washed with cold water until the washings are no longer acid to methyl orange. The washings are

added to the main portion of the aqueous liquid, which will contain the total alkali of the soap as nitrate; generally also small quantities of chloride and sulphate, soluble fatty acids if the soap is derived from cocoanut or palm kernel oils; glycerol in the case of soft soap or soap made by the cold process; and any sugar, glycerol, dextrin, gelatine or other soluble foreign matter which may have been added to the soap.

The funnel with the filter containing the insoluble acids is placed over a small weighed beaker in an air oven, and the whole is heated to about 100°. As the filter dries, the bulk of the melted acids will pass through it into the beaker below, where they may be weighed after cooling. The acids adhering to the filter and funnel a e washed by means of petroleum ether, which is completely volatile below 80°, into a tared flask, dried at 100° after removal of the solvent by evaporation, and weighed, their weight being added to that of the main portion. The weight of the total fatty acids, multiplied by 0·97, gives the weight of the acid anhydrides (or radicles) existing in the soap.

If a weighed portion of the acids is dissolved in neutral alcohol and titrated with standard potassium or sodium hydroxide solution, using phenol phthalein as indicator, the total combined alkali existing as soap proper may be found; this is calculated to $Na_2O$ or $K_2O$. The latter may also be found by subtracting the free alkali from the total alkali, determined as described below. The soluble fatty acids in the aqueous liquid, if any, are determined as described under (*e*) and added to the main portion in the final statement of the results of the analysis.

The valuation of soaps is largely based on the percentage of fatty acids, calculated to anhydrides, as indicated above. The best toilet soaps will contain

some 80 per cent. of fatty acids, good household soaps, 60 to 65 per cent. of fatty or fatty and rosin acids, while the cheaper grades which contain filling material, sodium carbonate or silicate, sand, etc., and the soft and hydrated soaps, may contain as little as 10 to 20 per cent. of fatty or fatty and rosin acids.

(*d*) *Total Alkali.*—The total aqueous liquid separated from the fatty and rosin acids, including the filtrate and washings obtained as described under (*c*), is titrated with semi-normal potassium or sodium hydroxide solution, using methyl orange as indicator. The difference between the number of cubic centimetres of normal nitric acid used for the liberation of the fatty acids as described under (*c*), and half the number of cubic centimetres of semi-normal alkali used in the last titration, will be the number of cubic centimetres of normal acid equivalent to the total alkali of the soap. This is calculated to $Na_2O$ or $K_2O$, as the case may be.

(*e*) *Soluble Fatty Acids.*—This estimation is based on the fact that the fatty acids show an acid reaction towards phenol phthalein but not towards methyl orange; the latter indicator may therefore be used for the estimation of free mineral acid by titration, in presence of fatty acids which may then be estimated by adding phenol phthalein to the solution which has previously been rendered neutral towards methyl orange, and continuing the titration with caustic alkali solution until a permanent pink tint appears. The determination of the soluble fatty acids is accordingly carried out by adding phenol phthalein to the solution from the determination of the total alkali (as described under (*d*)), and titrating with deci-normal caustic alkali solution. The number of cubic centimetres required to produce a permanent pink tint is calculated to caprylic

anhydride, $\begin{matrix} C_7H_{15} \\ C_7H_{15} \end{matrix}\!\!>\!O$, 2NaOH being equivalent to one molecule of the anhydride; the weight of the latter is added to the weight of the anhydrides of the insoluble acids already estimated as described under (*c*).

The presence of appreciable amounts of soluble fatty acids will indicate that the soap has been made from cocoanut or palm kernel oils.

(*f*) *Chlorides and Sulphates.*—These constituents may be determined in aliquot portions, say, one-fifth each, of the neutralised liquid obtained from operations (*d*) or (*e*). The chlorides are determined in the usual manner by titrating the faintly acid solution with deci-normal silver nitrate solution, using a few drops of potassium chromate solution as indicator, and continuing the titration until a permanent faint red-brown colour appears. The number of cubic centimetres of silver nitrate solution required is calculated to express the percentage of NaCl (or KCl) in the sample. Sulphates are determined by precipitation with barium chloride solution, in the usual manner, and the amount of barium sulphate weighed is calculated to express the percentage of $Na_2SO_4$ (or $K_2SO_4$) in the sample.

As will be seen from the table on p. 147, the better the quality of the soap, the smaller will be the percentage of sodium chloride and sulphate.

(*g*) *Glycerol* (in absence of sugar).—The determination of this constituent is mainly of interest in the case of soft soaps, and the hydrated soaps made by the cold process. As was pointed out above, some toilet soaps may contain added glycerol.

For the estimation, an aliquot portion of the neutralised solution obtained from operations (*d*) or (*e*) may be used. The method to be described is due to Hehner, and depends on the quantitative oxidation of glycerol to carbon dioxide and water by means of potassium

dichromate solution, the amount of dichromate used for the oxidation being measured by a titration process. The method is, of course, only applicable in the absence of other oxidisable matter such as sugar, which, if present, must be removed as described below under (*h*).

The following solutions will be required :—

*Potassium dichromate solution*, containing 74·56 grams of the pure salt and about 150 c.c. of concentrated sulphuric acid per litre.

*Ferrous ammonium sulphate solution*, containing 240 grams of $FeSO_4(NH_4)_2SO_4 6H_2O$ and 50 c.c. of concentrated sulphuric acid per litre.

*Potassium dichromate solution of exactly one-tenth the strength of the other solution of the same salt.* The stronger dichromate solution, 1 c.c. of which should be equivalent to 0·01 gram of glycerol, is titrated against the ferrous ammonium sulphate solution.

The solution in which the glycerol is to be estimated is made up to about 250 c.c. and transferred to a beaker which has been cleaned with potassium dichromate and sulphuric acid, in order to remove all traces of oxidisable matter. 50 c.c. of the stronger dichromate solution are then added, and the beaker is covered with a clock glass and heated for 2 hours in boiling water. At the end of this time an excess of the ferrous ammonium sulphate solution is added, so that the whole of the remaining potassium dichromate will be reduced to chromic sulphate, and a convenient amount of the ferrous salt left over for titration with the weaker dichromate solution. The approximate quantities of the various solutions required may be calculated from the following equation, representing the interaction between the dichromate and the ferrous salt in solution.

$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7H_2O.$$

The titration with potassium dichromate solution is carried out, using a weak solution of potassium ferricyanide as an outside indicator, according to the well-known method described in text books of quantitative inorganic analysis. As previously stated, the glycerol is quantitatively oxidised to carbon dioxide and water by the potassium dichromate, which is reduced to chromic sulphate as indicated by the equation given above. From these data the amount of glycerol present in the original solution may be calculated.

(*h*) *Glycerol and Sugar in presence of one another.*—Cane sugar is sometimes added to the cheaper or inferior grades of toilet soaps, in which it may be present to the extent of 20 to 30 per cent.

The estimations described under this heading are carried out on an aliquot portion of the neutralised solution obtained from operations (*d*) or (*e*). Carbohydrates may be tested for in a small portion of this solution by adding a few drops of an alcoholic solution of $\alpha$ naphthol and then 1 or 2 c.c. of concentrated sulphuric acid; in the presence of carbohydrates, a violet coloration will be formed at the point of contact of the acid and aqueous layers. The presence of cane sugar may be inferred if a small portion of the solution shows a marked increase in its action on Fehling's solution (see "Estimation of Cane Sugar" below), after heating for about 10 minutes in boiling water with about one-tenth its volume of concentrated hydrochloric acid. If, however, the sugar present is glucose or invert sugar, as may occasionally be the case, a pronounced action on Fehling's solution will be obtained at once. It should be remembered that glycerol reduces Fehling's solution to some extent on prolonged heating; in the presence of sugars, however, a marked reducing action should be apparent

after warming from half a minute to a minute. Sugar, although oxidisable by potassium dichromate, cannot be quantitatively estimated by means of this reagent; if, therefore, the glycerol is to be estimated by the method just described, it must first be separated from the sugar. According to Donath and Meyer, this may be accomplished as follows:—

Add to the solution slaked lime in sufficient quantity to combine with the whole of the sugar present, allowing at least 3 molecules of calcium hydroxide to each molecule of sugar; for this purpose, 1 to 2 grams of the pure hydroxide should be sufficient; further add an equal quantity of washed and ignited sand, boil the liquid down to a syrup, pulverise the solidified residue, and exhaust it in a corked flask with 80 to 100 c.c. of a mixture of equal parts of ether and alcohol. The glycerol will pass into solution while the sugar will remain undissolved. After filtering and cautiously removing the solvent by evaporation, the residual glycerol is dissolved in about 200 c.c. of water and estimated as described above in the previous section (*g*). In order to avoid loss of glycerol by evaporation, it should not be heated too strongly during the removal of the solvent. On the other hand, the alcohol and ether, being oxidisable by potassium dichromate, must be entirely removed.

*Estimation of Cane Sugar.*—The method commonly employed for the gravimetric estimation of sugars is based on the fact that the members of this class, which contain free carbonyl groups in the molecule, have the power of reducing an alkaline solution of copper (see the preparation of Fehling's solution below) with the precipitation of cuprous oxide. The ratio between the amount of cuprous oxide formed and the weight of the reducing sugar cannot be expressed by definite chemical

equations, and, moreover, varies with the experimental conditions as well as with the amount of sugar taken. If, however, the determination is carried out under certain standard conditions, the amount of sugar corresponding to a given weight of precipitated cuprous oxide may be ascertained from the tables of ratios which have been determined for each individual sugar. Cane sugar is a disaccharide which contains no free carbonyl group in the molecule ; it consequently differs from lactose, maltose, glucose, fructose and galactose in forming no osazone and having no action on an alkaline copper solution such as Fehling's solution. On heating in aqueous solution with a little mineral acid, cane sugar is hydrolysed with the formation of glucose and fructose in accordance with the following equation :—

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

The resulting mixture is known as invert sugar, and the process is referred to as the inversion of cane sugar, owing to the change in sign of the optical rotation of the solution, from positive to negative, which it occasions. A method for the estimation of cane sugar, based on this latter change, is sometimes employed, Invert sugar, as will be gathered from what has already been said, reduces Fehling's solution, and the amount of cuprous oxide formed under given conditions may be taken as a measure of the amount of cane sugar originally present in the solution.

The determination of cane sugar in soap may be carried out on an aliquot portion of the neutralised solution from operations (*d*) or (*e*). The glycerol need not be removed, provided that the solution is sufficiently dilute, and the heating with the Fehling's solution is not unduly prolonged. Under these conditions the

reducing action of the glycerol will be negligible, for the purposes of a technical analysis.

The Fehling's solution, which will be required for the determination, according to the directions of Brown, Morris and Millar (*J.C.S.*, 1897, lxxi., p. 278), is prepared as follows: 173 grams of Rochelle salt (sodium potassium tartrate) and 65 grams of pure anhydrous sodium hydroxide are dissolved in water and made up to 500 c.c.; 34·6 grams of pure crystallised copper sulphate, $CuSO_4\,5H_2O$, are dissolved in a separate quantity of water and the solution made up to 500 c.c. The two solutions are kept separately, and mixed in equal quantities when required for use.

The inversion is carried out by heating the sugar solution with one-tenth its volume of fuming hydrochloric acid for 15 minutes in a water bath at 68° C., as indicated by a thermometer placed in the liquid itself.

The amount of sugar used in the determination should be regulated so that the amount of copper weighed is from 0·15 to 0·35 gram (or the corresponding amount of cupric oxide). For this, about 10 to 30 c.c. of a 1 per cent. solution of invert sugar will be required. In order to ascertain the approximate amount of the sugar solution required, a preliminary rough determination of its strength may be made as follows: 10 c.c. of the mixed Fehling's solution and 10 c.c. of distilled water are placed in a small flask and heated to boiling, while the inverted sugar solution is run in from a burette until the copper is completely precipitated. The end point of the titration is reached when the blue colour has just been discharged, and a drop of the clear solution placed on a piece of pure filter paper beside a drop of potassium ferrocyanide solution acidulated with acetic acid produces no brown stain

at the point where the liquids meet. The titration should be performed as rapidly as possible to avoid the cuprous oxide redissolving owing to atmospheric oxidation; it is, therefore, best to verify the first titration by a second, in which practically the whole of the sugar solution required is added at once, and the solution boiled for 2 minutes before testing for copper. Having thus roughly determined the strength of the sugar solution relatively to the Fehling's solution, the latter is standardised in exactly the same way as just described, against a ½ per cent. solution of cane sugar which has been inverted as described above.

The actual determination is carried out as follows: 25 c.c. of each of the Fehling's solutions are placed in a beaker of about 200 c.c. capacity, and the mixture is diluted with distilled water so that after the addition of the sugar solution the total volume will be 100 c.c. The beaker is covered with a clock glass and heated in boiling water. After a few minutes an accurately measured portion of the sugar solution is added, the heating is continued for exactly 12 minutes, and the precipitated cuprous oxide filtered off on a Gooch crucible without delay. The precipitate is well washed with hot water, then with a little alcohol, followed by ether, and dried in an oven. The cuprous oxide is then ignited to cupric oxide in the Gooch crucible, the latter being placed in an ordinary crucible which is heated over a Bunsen flame. The cupric oxide is weighed, and converted to sugar by referring to the table on p. 141. A blank test should be made on 50 c.c. of the mixed Fehling's solution, and any cuprous oxide formed here deducted from the amount weighed in the actual determination.

From the accompanying table, the amounts of

glucose, fructose or invert sugar corresponding to given weights of copper may be found. Intermediate values may be arrived at by interpolation. The weight of invert sugar, multiplied by 0·95, will give the corresponding weight of cane sugar. The factor for converting CuO to Cu is 0·7989.

In some cases it may happen that the soap contains nvert sugar or glucose. These may be determined exactly as described above, omitting the heating with hydrochloric acid. Any increase in the amount of cuprous oxide precipitated after treatment with hydrochloric acid would be due to cane sugar.

TABLE FOR FINDING AMOUNTS OF GLUCOSE, AND INVERT SUGAR, CORRESPONDING TO GIVEN WEIGHTS OF COPPER, OBTAINED BY THE METHOD OF BROWN, MORRIS AND MILLAR (*Journ. Chem. Soc.*, Vol. 71, p. 281).

| Glucose Grams. | Copper Grams. | Glucose Grams. | Copper Grams. | Invert Sugar Grams. | Copper Grams. | Invert Sugar Grams. | Copper Grams. |
|---|---|---|---|---|---|---|---|
| 0·050 | 0·1030 | 0·155 | 0·3020 | 0·050 | 0·0975 | 0·155 | 0·2915 |
| 0·055 | 0·1134 | 0·160 | 0·3103 | 0·055 | 0·1076 | 0·160 | 0·3002 |
| 0·060 | 0·1238 | 0·165 | 0·3187 | 0·060 | 0·1176 | 0·165 | 0·3086 |
| 0·065 | 0·1342 | 0·170 | 0·3268 | 0·065 | 0·1275 | 0·170 | 0·3167 |
| 0·070 | 0·1443 | 0·175 | 0·3350 | 0·070 | 0·1373 | 0·175 | 0·3251 |
| 0·075 | 0·1543 | 0·180 | 0·3431 | 0·075 | 0·1468 | 0·180 | 0·3331 |
| 0·080 | 0·1644 | 0·185 | 0·3508 | 0·080 | 0·1566 | 0·185 | 0·3410 |
| 0·085 | 0·1740 | 0·190 | 0·3590 | 0·085 | 0·1662 | 0·190 | 0·3490 |
| 0·090 | 0·1834 | 0·195 | 0·3668 | 0·090 | 0·1755 | 0·195 | 0·3570 |
| 0·095 | 0·1930 | 0·200 | 0·3745 | 0·095 | 0·1848 | 0·200 | 0·3650 |
| 0·100 | 0·2027 | 0·205 | 0·3822 | 0·100 | 0·1941 | 0·205 | 0·3726 |
| 0·105 | 0·2123 | — | — | 0·105 | 0·2034 | | |
| 0·110 | 0·2218 | — | — | 0·110 | 0·2128 | | |
| 0·115 | 0·2313 | — | — | 0·115 | 0·2220 | | |
| 0·120 | 0·2404 | — | — | 0·120 | 0·2311 | | |
| 0·125 | 0·2496 | — | — | 0·125 | 0·2400 | | |
| 0·130 | 0·2585 | — | — | 0·130 | 0·2489 | | |
| 0·135 | 0·2675 | — | — | 0·135 | 0·2578 | | |
| 0·140 | 0·2762 | — | — | 0·140 | 0·2662 | | |
| 0·145 | 0·2850 | — | — | 0·145 | 0·2750 | | |
| 0·150 | 0·2934 | — | — | 0·150 | 0·2832 | | |

Although results of very great accuracy are not required in the present instance, the method has been described in detail as it will be referred to in connection with work to be described in subsequent chapters.

(*i*) *Free Caustic Alkali or Fatty Acids.*—According to Hope, 10 to 30 grams of the original sample are dissolved in hot absolute alcohol in a flask, loosely corked to prevent absorption of moisture and carbon dioxide from the air. If the soap contains much water, it should first be partially dried in an atmosphere free from carbon dioxide. The hot solution is filtered rapidly to prevent undue exposure of the solution to air, care being taken that none of the soap jelly separates out on the filter. The filter is washed with absolute alcohol, and the total filtrate and washings titrated in presence of phenol phthalein with deci-normal acid or alkali, according to its reaction. If alkaline, the amount of standard acid required will give the percentage of free caustic alkali in the soap; if acid, the amount of alkali required is calculated to oleic acid ($C_{18}H_{34}O_2$) and returned as free fatty acids.

Toilet soaps should be entirely free from caustic alkali, while in laundry soaps the percentage of this constituent should not be above ½ per cent.

By titrating the neutralised alcoholic solution with acid, using this time methyl orange as indicator, the alkali existing in the soap as sodium salts of fatty or rosin acids may be found. (See also (*d*).)

(*j*) *Alkaline Carbonate, Silicate, etc.*—The residue left on the filter contains any carbonate, silicate, borate, aluminate, etc., together with other insoluble material such as starch, sawdust, sand, pumice, chalk, insoluble colouring matter, etc., which may have been present in the soap. The alkaline carbonate, silicate, borate or

aluminate is separated from the residue insoluble in alcohol by extracting with cold water and filtering. One half of the filtrate may then be titrated with deci-normal sulphuric acid in presence of methyl orange as indicator, in order to find the amount of soda present, while the other half may be evaporated to dryness and the nature of the alkaline material determined by examining the residue by the usual methods of qualitative inorganic analysis.

In a good toilet soap, the amount of alkaline carbonate should not exceed ½ per cent. In laundry, scouring and marine soaps, the addition of larger amounts of alkaline carbonate or silicate may be quite permissible.

(*k*) *Insoluble Residue from* (*j*).—The residue left on the filter after extracting the alkaline material with water, may be dried, weighed and further examined. The substances mentioned above (p. 127) will readily be recognised by the usual tests, as well as their appearance.

*Total Alkali and Nature of the Same.*—By titrating an aqueous solution of a known weight of the soap with standard acid, using methyl orange as indicator, the total alkali present in the soap may be found. This should agree with the sum of the determinations of alkali as (1) free hydroxide, (2) free carbonate, or silicate borate, etc., and (3) combined as soap with fatty or rosin acids.

If it is desired to determine the nature of the alkali, *i.e.*, whether soda or potash or a mixture of these, the alcoholic soap solution neutralised to methyl orange from operation (*j*) is treated with baryta solution until alkaline to phenol phthalein, and barium chloride solution is added as long as precipitation occurs. After filtering, the solution is evaporated to dryness, and the residue examined qualitatively or quantitatively for

sodium or potassium by any of the usual methods described in the text-books on qualitative and quantitative inorganic analysis.

(*l*) *Detection and Estimation of Rosin Acids.*—Rosin acids may be detected by the Liebermann Storch reaction as follows: a small portion of the acids, precipitated and separated as described under (*c*) is dissolved in acetic anhydride at a gentle heat, and the solution allowed to cool. Sulphuric acid of specific gravity 1·53, prepared by adding 34·7 of the concentrated acid to 37·5 c.c. of water, is very carefully added when, in the presence of rosin acids, a reddish violet coloration will be developed. If the acid is not added with sufficient care, the mixture will become too warm, with the result that the coloration will not be observed, a brownish-yellow coloration being developed at once. Lewkowitsch points out that cholesterol gives a similar reaction to that obtained with rosin acids, and recommends that if the presence of this substance is suspected, it should be removed by extracting the aqueous soap solution with ether before liberating the acids for the test. As has been pointed out in the previous chapter on the fatty oils and fats, cholesterol is the principal unsaponifiable constituent of the animal fats.

For the estimation, the mixture of fatty and rosin acids isolated as described under (*c*), may be used. The method of Twitchell depends on the fact that while the fatty acids are esterified on treatment with hydrogen chloride in alcoholic solution, the rosin acids are unchanged, and may be estimated by titration with standard alkali solution in presence of phenol phthalein as indicator.

2 to 3 grams of the mixed fatty and rosin acids are dissolved in 10 times their volume of alcohol, in a flask,

and dry hydrogen chloride gas is bubbled through the solution until no further absorption takes place. The process will be complete in about 45 minutes, when the ethyl esters of the fatty acids will have separated as an oily layer floating on the alcohol. The liquid is now diluted with five times its volume of water and boiled till the acid solution is clear, the esters containing the rosin acids in solution floating on the top. The whole is transferred to a separating funnel by means of ether, and the ethereal layer is washed with water till all the mineral acid has been extracted from it; this will be accomplished when the aqueous layer no longer reacts acid towards methyl orange, or gives a precipitate or opalescence with silver nitrate solution in presence of nitric acid. The ethereal layer is now transferred to a flask, 50 c.c. of alcohol, neutralised towards phenol phthalein, are added, and the mixture is titrated with standard sodium hydroxide solution, using phenol phthalein as indicator. The titration should not be unduly prolonged, or partial hydrolysis of the esters by excess of alkali may take place. From the number of cubic centimetres of alkali solution required for neutralisation, the amount of the rosin acids may be calculated, assuming their combining weight to be 346.

As mentioned above, rosin should only be present in the cheaper grades of soap; a good laundry soap should only contain about 20 per cent. of rosin acids.

(*m*) *Origin of the Fatty Acids.*—It will not often be necessary to determine the nature of the fat from which the soap is derived. As mentioned above, if an appreciable quantity of soluble fatty acids is found by the process described under (*e*), the soap probably contains fatty acids derived from cocoanut or palm kernel oils. In some cases it may be possible to determine the origin of the fatty acids by determining such constants as the

solidifying point (titer test), saponification value, iodine value and specific gravity, as described in Chapter III. The problem is, however, usually not an easy one, and becomes decidedly complicated if rosin acids are present, or mixtures of fats have been used. Further, the fats used in the manufacture of the soap may in some cases have been bleached by potassium dichromate and hydrochloric acid or similar mixtures, when the value of the indications afforded by the methods just alluded to, especially the iodine value, will be considerably lessened.

*The Results of the Analysis.*—The accompanying tables contain typical analyses of various grades of soap, most of which are by C. Hope. As a rule, the most important of the determinations described above are those of water, alkali combined as soap, to be calculated as $Na_2O$, free caustic alkali as NaOH (or KOH), sodium (or potassium) carbonate, water insoluble material, *i.e.*, fillers or adulterants (see under (*k*)), fatty acids, calculated as anhydrides, and rosin acids.

## The Determination of Phenols and Neutral Hydrocarbons in Carbolic Soaps.

The following method for the analysis of carbolic soaps is due to Allen: 5 grams of the sample are dissolved in warm water, and 20 to 30 c.c. of a 10 per cent. solution of sodium hydroxide, according to the amount of phenols supposed to be present, are added. The alkaline solution is transferred to a separating funnel and extracted with ether. The ethereal solution is evaporated in a tared flask on the water bath, and the residue weighed; this residue, which will consist of neutral oils of tar or other substances of a like nature which may have been added to the soap, may be appreciably volatile at 100°, in which case it will be difficult to get an accurate estimate of its amount.

The alkaline liquid which has been separated from the ether is then transferred to a more capacious separating

| Description. | Fatty and Rosin Anhydrides. | $Na_2O$ as Soap. | $Si_2O$. | $Na_2O$ as Silicate. | $Na_2CO_3$ and NaOH. | NaCl. | $Na_2SO_4$. | CaO and $Fe_2O_3$. | $H_2O$. | Total. | Fatty and Rosin Acids. | Origin. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| White I. . . | 69·06 | 8·96 | 0·01 | *nil* | 0·27 | 0·49 | 0·16 | 0·07 | 21·14 | 100·18 | 71·20 | Tallow. |
| White IV. . | 44·27 | 6·23 | 7·02 | 2·36 | 0·75 | 0·32 | 0·34 | 0·34 | 38·14 | 99·77 | 45·64 | Tallow and cocoanut oil. |
| Cold water I. . | 71·30 | 7·98 | 1·07 | 0·48 | 0·75 | 0·36 | 0·30 | 0·16 | 17·44 | 99·84 | 73·50 | Tallow, rosin and cotton oil. |
| Cold water II. | 49·95 | 7·00 | 2·34 | 1·01 | 0·33 | 0·51 | *nil* | 0·50 | 38·18 | 99·82 | 51·50 | Tallow, rosin and cotton oil. |
| Marseilles I. . | 62·66 | 7·27 | 0·06 | 0·03 | 0·77 | 0·76 | 0·30 | 0·16 | 28·20 | 100·21 | 64·60 | Chiefly olive oil. |
| Palm oil I. . | 59·28 | 6·65 | 0·42 | 0·01 | 0·39 | 0·47 | 0·13 | 0·16 | 32·35 | 99·86 | 61·08 | Palm oil. |
| Mottled . . | 38·89 | 5·76 | 6·40 | 1·29 | 1·62 | 1·78 | 0·72 | 0·03 | 38·70 | 95·19 | 40·10 | Palm kernel oil. |
| Pale rosin I. . | 60·90 | 7·22 | 0·04 | *nil* | 0·10 | 0·46 | 0·12 | 0·02 | 31·22 | 100·08 | 62·78 | Tallow and rosin. |
| Pale rosin III. | 39·92 | 4·70 | 0·62 | 0·25 | 0·20 | 1·48 | 0·18 | 0·15 | 52·40 | 99·90 | 41·15 | ditto. |
| "Yellow" for foreign markets | 10·90 | 1·36 | 0·03 | *nil* | trace | 2·57 | 0·56 | 0·14 | 84·00 | 99·56 | 11·20 | ditto. |
| Marine for emigrants . | 19·42 | 3·11 | 9·00 | 3·98 | 3·00 | 5·13 | 0·35 | 0·16 | 53·52 | 97·47 | 20·02 | Palm kernel oil. |
| White Castille | 76·7 | 9·14 | — | — | — | 0·36 | — | 0·09 | 13·25 | 100·54 | — | — |

funnel and treated with an excess of saturated brine, which will precipitate the soaps while the phenols remain in solution. After agitating to coagulate the soap, the liquid is filtered; in case the soap should not coagulate easily, the addition of a little tallow or palm oil soap dissolved in water, will often facilitate the separation. The precipitated soap is washed twice with strong brine, and the washings are added to the main filtrate which is then diluted to 1 litre. 100 c.c. of this solution, which will be equivalent to 0·5 gram of soap, are placed in a 500 c.c. stoppered bottle and acidulated with sulphuric acid, when it should remain perfectly clear; if precipitation occurs at this stage, the fatty acids will not have been completely removed. In such cases 200 c.c. of the alkaline liquid should be taken, and powdered salt dissolved in it to saturation; the solution thus obtained should then be filtered through a dry filter, and 100 c.c. of the filtrate acidified as before. The phenol is then determined by titration with standard bromine water (see below), which is run in from a burette, the stopper of the bottle being replaced and the contents agitated after each addition. The end point is reached when the solution acquires a permanent faint yellow tint. If crystallised phenol has been introduced into the soap the precipitated tribromophenol will be precipitated in snow-white flocks which allow the faintest tint owing to excess of bromine to be observed quite readily. If, on the other hand, cresylic acid, *i.e.*, the cresols, has been added, the precipitate will be milky and will not separate well from the liquid, though the end point can still be observed. The addition to the original solution of a known amount of pure phenol may cause the precipitate to coagulate, in which case the yellow colour due to excess of bromine will be more

easily seen. This addition must, of course, be allowed for in calculating the result of the analysis.

The bromine solution which is used for the titration is conveniently prepared by mixing in a stoppered bottle one measure of saturated bromine water with two measures of water. The resulting solution, which is approximately of 1 per cent. strength, should be standardised immediately after use by means of a standard solution of phenol of the quality indicated by the analysis to be present in the sample. The phenol solution may be made by dissolving 0·5 gram of the phenol (usually either Calvert's No. 2 or No. 5 carbolic acid) in 20 c.c. of a 10 per cent. solution of sodium hydroxide with 5 grams of a non-phenolic soap. The solution is precipitated with brine in the same way as the solution of the sample under examination, the filtrate diluted to one litre, and 100 c.c. acidulated with sulphuric acid and titrated with the bromine water.

Carbolic soaps are often sold as containing 20 or 30 per cent. of carbolic acid; they may contain anything from 1 to 30 per cent. of phenol, derived either from pure crystallised phenol or the common cresylic acids. According to Allen, the proportion of phenol found is occasionally less than that stated to be present, the difference probably being due to loss by evaporation.

### Phenolic Disinfectants containing Soap.

The preparations to be dealt with under this heading consist of creosote oil or coal tar phenols, chiefly cresols (cresylic acid), to which soap has been added in order to form an emulsion or a homogeneous product which shall be readily miscible with water. As examples we may take the preparations known as creoline and lysol. The former consists of creosote oil and an aqueous solution of soda rosin soap, which have been mixed to form an emulsion. Being made from the crude creosote

oil, it contains some 40 to 60 per cent. of neutral hydrocarbons and about 10 to 20 per cent. of cresylic acid; the better the quality, the less of the former and the more of the latter will it contain. Creoline should form a permanent emulsion when mixed with water in the proportion of 1 to 40, the greater part of the cresylic acid dissolving as such, or as sodium salts, and the neutral hydrocarbons remaining suspended in the form of minute globules owing to the emulsifying action of the soap. Lysol and sapocarbol, on the other hand, are prepared by mixing cresylic acid containing relatively small amounts of hydrocarbons, with rosin or a fatty oil such as linseed oil, and saponifying the rosin or oil by treating the mixture with a solution of potash in water and alcohol. The viscous brown transparent liquid thus obtained is readily soluble in water. Lysol should contain at least 40 to 50 per cent. of phenols, and at most only about 3 or 4 per cent. of hydrocarbons, in order that it may dissolve in water as completely as possible.

Besides the products just described, there are a number of other similar preparations on the market containing varying proportions of cresylic acid, soap and hydrocarbons. Among these may be mentioned sanatol, saprol, solutol and salveol. Many sheep dips are similar in composition to the above, and may be analysed by the methods given below. The latter preparations sometimes contain sodium arsenate or sodium carbonate in addition to or in place of the soap.

*The Analysis of Creoline, Lysol, Sheep Dips, etc.*—The estimation of neutral oils of tar, coal tar phenols, pyridine bases and fatty or rosin acids may be carried out as follows: 20 grams of the sample are made distinctly acid by the addition of dilute sulphuric acid (1 to 5), and agitated with ether in a separating funnel; after separating, the aqueous layer is again extracted with two successive portions of ether. The pyridine bases may be estimated in the acid liquid, as described in Chapter II., under the "Testing of Creosoting Liquor."

The ethereal extracts, containing the hydrocarbons, phenols and fatty or rosin acids, are united and extracted with three successive portions of 50 c.c. of a 10 per cent. solution of sodium hydroxide; the phenols and acids are thus removed from the ether, which retains only the hydrocarbons in solution. The alkaline extracts are united and extracted once or twice with ether in order to free them from all traces of suspended hydrocarbons; all the ethereal extracts are then united, dehydrated by means of calcium chloride and evaporated in a small tared flask on the water bath. The residue is dried at 100° and weighed as hydrocarbons. The alkaline liquid is acidified with dilute sulphuric acid, allowed to cool, and the liberated acids and phenols are removed by shaking out several times with ether. The separation of the phenols and the acids contained in solution in the ether is accomplished by shaking out the latter with dilute sodium carbonate solution, which will extract only the acids as sodium salts. The acids may then be liberated by the addition of dilute sulphuric acid to the alkaline solution, and separated and estimated as described in the present chapter under (*c*). If desired, they may be examined for rosin acids, as described on p. 144. The ethereal extract, which has been shaken out with sodium carbonate solution till all the acids have been removed, contains the phenols; it may be evaporated in a tared flask on the water bath, and the residue dried at 100° and weighed.

Soda or potash may be estimated by burning off about 5 grams of the original sample in a platinum crucible or dish, treating the residue with successive small portions of concentrated sulphuric acid, and weighing the ignited sodium or potassium sulphate in the usual manner.

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## CHAPTER V

### PETROLEUM AND ITS DISTILLATION PRODUCTS—LUBRICATING OILS

#### INTRODUCTORY.

THE petroleums, or mineral oils, are usually more or less viscous, dark brown or black fluids having specific gravities lying between 0·73 and 0·97. Chemically, they consist of complex mixtures of hydrocarbons together with smaller quantities of oxygen, nitrogen and sulphur compounds; the nature of the hydrocarbons varies with the locality from which the petroleum is obtained, and, to a lesser degree, with the age of the well. Most petroleums distil over a wide range of temperature and yield a variety of important products such as motor spirit, burning oil, lubricating oil, etc., while the residues which remain after distilling off the more volatile portions have in recent years found a most important use as fuel for internal combustion engines.

*Composition of the Petroleums.*—As examples, we may take the petroleums of Pennsylvania, U.S.A., and the Caucasus, which together constitute by far the greater part of the world's supply of this commodity.

Pennsylvania petroleum, which usually has a specific gravity lying between 0·80 and 0·87, consists chiefly of paraffins from pentane $C_5H_{12}$ (b.p. 38°) up to the solid $C_{20}H_{42}$; higher members of the series, such as $C_{25}H_{52}$ and $C_{30}H_{62}$, are also known to be present. The portions boiling above 200° probably contain olefines in addition to the paraffins; as is also the case with the other petroleums, many of the higher boiling constituents are of unknown constitution. Aromatic hydrocarbons are present only in small amount. Pennsylvania petroleum is accompanied by hydrogen and the members of the

paraffin series which are gaseous at the ordinary temperature.

Caucasian petroleum has a higher specific gravity than Pennsylvania petroleum, usually from 0·88 to 0·94, and differs widely from the latter in chemical composition. According to Markownikoff, it contains at least 80 per cent. of naphthenes, *i.e.*, polymethylenes and their alkyl derivatives, among which pentamethylene, hexamethylene, methyl hexamethylene and other similar compounds of known constitution have been recognised. The naphthenes resemble the paraffins in being saturated bodies which are not acted on by concentrated sulphuric acid or potassium permanganate ; with the halogens and dilute nitric acid, they yield halogen and nitro substitution products. In addition to the naphthenes, Russian petroleum contains about 10 per cent. of aromatic hydrocarbons, and less than 1 per cent. of paraffins. The higher boiling fractions appear to contain unsaturated substances such as olefines and naphthylenes, the latter being olefine analogues of the naphthenes. Like Pennsylvania oil, Russian oil contains a number of substances of unknown constitution, especially in the higher boiling fractions.

From the foregoing it will be gathered that the two classes of petroleums described show important differences in their behaviour on distillation. Generally speaking, Pennsylvania petroleum distils over a wider range of temperature, and contains a much larger proportion of volatile matter than Russian petroleum, the residue from the latter being larger in amount and more fluid in consistency than that from the former. The primary products of distillation of the petroleums are as follows : (1) Light oils or mineral naphtha, from which are obtained by fractional distillation various mixtures of light hydrocarbons which are used as fuel for motor engines, extraction and cleaning purposes, and burning naphtha. (2) Illuminating oils, such as kerosene or solar oil. (3) Residuum, which in the case of Russian oils is generally used as fuel, and in the case of Pennsylvania oil, distilled under vacuum or ordinary pressure for lubricating oils, the residue in the latter case being

worked up for vaseline, solid paraffins or paving asphalt. If the distillation is carried to a finish, the residue consists of a coke-like material which may be used as fuel.

The method of distillation depends on the nature of the petroleum and the nature of the products required. Russian petroleum is distilled by the continuous process, the material passing through a series of stills kept at progressively increasing temperatures; the distillate is divided into two portions, gasolene and kerosene. The former is redistilled till the distillate has a specific gravity of 0·750, and the residue added to the main kerosene fraction, which is distilled till the specific gravity of the distillate reaches about 0·825. The total residue, which has a specific gravity of 0·903, if distilled, will yield about 10 per cent. of solar oil, of specific gravity 0·806 and flash point 105° F., as determined by the Pensky-Martens apparatus, and about 35 per cent. of lubricating oils, the final residue being used as fuel. Compared with Pennsylvania petroleum, Russian petroleum yields a relatively small proportion of light petroleum and burning oil, the yield of the former, which includes benzine of specific gravity about 0·725, and heavy benzine or gasolene of specific gravity about 0·770, being about 4 to 6 per cent., and of burning oils, about 27 per cent. of kerosene of specific gravity about 0·822 and 5 per cent. of solar oil of specific gravity about 0·86 to 0·88. At Baku, about 30 to 40 per cent. is generally distilled off, the residue, known as "astatki," being used as liquid fuel.

Pennsylvania petroleum cannot be distilled by the continuous process, owing to the large amount of burning oil which it yields, and the viscous nature of the residue. When submitted to the simple distillation process, it first yields gaseous paraffins which are either burnt as fuel or condensed by artificial cooling; the liquid products thus obtained, *i.e.*, cymogene, b.p. 32° F., and rhigolene, b.p. 65° F., are used in surgery.[1] The light petroleum

[1] Distinction must be made between benzine, which is obtained from petroleum or mineral naphtha, and benzene, the aromatic hydrocarbon obtained from benzol, the distillation product of coal tar naphtha. The terms petroleum spirit and light petroleum are also used to designate the more volatile distillation products of petroleum naphtha.

or petroleum naphtha fraction is taken till the specific gravity of the distillate reaches 0·725 to 0·750; it includes petroleum ether, specific gravity 0·625, gasolene, specific gravity 0·665, naphtha, specific gravity 0·676, and benzine, specific gravity 0·736, amounting to 9 to 18 per cent. of the total. The kerosene fraction is taken until the specific gravity of the distillate reaches 0·840 to 0·845, the average yield of burning oils being about 55 per cent. The residue is transferred to other stills and distilled for lubricating oils, the average yield of the latter, if distilled under ordinary pressure, being about 17 per cent. The solid paraffin amounts to about 2 per cent., and coke residue about 10 per cent. Distillation of the residue by the vacuum process gives a much larger yield of lubricating oils and vaseline. Sometimes the heavier oils are "cracked" after removal of the naphtha. In this process the vapours are allowed to condense on the walls of the still, and on falling back into the hot residue, decomposed with the formation of lower boiling substances. The yield of burning oils may thus be increased, it being possible to obtain about 75 per cent. of oil flashing at 20° C., as indicated by the Abel apparatus, though the yield of higher class oils of higher flash point is smaller.

Regarding the petroleums from other parts of the world, the Galician and Roumanian oils are intermediate between the Pennsylvania oils on the one hand, and the Russian oils on the other, in respect to chemical composition and general properties. The specific gravity of these oils is usually about 0·870. The petroleums obtained from Germany and Ohio, U.S.A., also contain both paraffins and naphthenes. Californian petroleum contains only a small percentage of low boiling constituents; it contains no paraffins, but naphthenes and aromatic hydrocarbons, the latter often being present in considerable amount. Appreciable quantities of oxygen and nitrogen compounds are also present. Texan petroleum does not, as a rule, commence to distil below 240°, and consists chiefly of unsaturated hydrocarbons of high molecular weight. Canadian petroleum contains paraffins and olefines, more aromatic hydro-

carbons and less light paraffins than Pennsylvania oil.

The greater part of the world's supply of burning oil and light petroleum, or benzine, is obtained from the American, and some of the Roumanian and Galician oils. The lubricating oils obtained from these are generally heavier, more viscous and of higher solidifying point than those obtained from the Russian oils. Oils for lubricating steam cylinders, which require to be fairly thick and viscous on account of the relatively high temperatures at which they are used, are therefore obtained best from the American petroleums. Crude petroleums containing little or no volatile hydrocarbons, coming under the heading of light petroleum or burning oils, will, no doubt, find increasing use as liquid fuel for internal combustion engines of the Diesel type, the only preparation necessary being the removal of water and solid matter by the settling out process to which crude oils are generally subjected. The use of Russian petroleum residue as liquid fuel has already been alluded to.

The various fractions obtained by the distillation of crude petroleum are refined, where necessary, by treatment with limited quantities of concentrated sulphuric acid, and subsequent washing with dilute caustic soda solution and water. Impurities which colour the oil and give it an objectionable odour are thus removed. If sulphur compounds are present in appreciable quantity, they are removed generally by treatment with lead or copper oxide ; either the fractions are redistilled over the metallic oxide, or the vapours are allowed to pass over the latter. In Canada, burning oils are desulphurised by treatment with a solution of litharge in caustic soda solution.

### The Examination of Crude Petroleum.

Owing to the complex nature of crude petroleums, these are but rarely examined by purely chemical methods in technical laboratories. By means of the distillation test, described below, the nature and

amount of the distillate to be expected may be determined, and the oil may be roughly classified. The specific gravity may also be used to help in classifying and comparing petroleums. The determination of extraneous matter, *i.e.*, water and sediment, will also be described.

*Water.*—A weighed quantity of the oil, about 100 to 200 grams, is mixed with about a third of its bulk of xylene, and distilled from a flask heated in an oil bath; the distillate is collected in a graduated cylinder or vessel of the form shown in the accompanying illustration. The distillation is stopped when no more water is seen to come over, and the vessel containing the distillate is warmed and gently shaken so that the water adhering to the sides falls to the bottom. The volume of the layer of water at the bottom of the cylinder or in the constricted part of the special measuring vessel is read off after cooling.

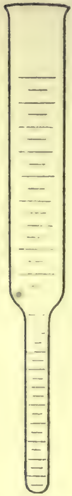

FIG. 9.—Measuring Vessel for Water in Petroleum.

*Sediment.*—5 to 10 grams of the oil are well mixed with 100 to 500 grams of benzene and allowed to stand overnight; the benzene and petroleum mixture is then filtered through a weighed filter, and the insoluble residue washed with benzene, dried at 100° and weighed. The sediment estimated will consist of mineral matter, and will not include any solid pitch or asphalt which may exist in the oil, these being soluble in benzene.

*Specific Gravity.*—If the oil is not too thick, a hydrometer may be used. The oil is poured into a cylinder of suitable size and allowed to stand for some time to

acquire the room temperature. The float is allowed to sink gradually into the oil, and its level read after 15 minutes, the reading corresponding with the level of the liquid being taken. In the case of dark oils, the level to which the oil rises up the stem of the float is read off, and 0·0015 or 0·0010 is added to the reading, according as the paper scale is shorter or longer than 16 cm. The temperature may be read off from the thermometer on the float, or, failing this, the room temperature may be taken. In order to reduce the reading to 15°, a correction of 0·00065 per degree Centigrade may be applied.

If the specific gravity bottle is used, and the oil is thick, the bottle should first be nearly filled with the oil and allowed to stand in a warm place overnight, in order that all air bubbles may rise to the top. The bottle and its contents are then cooled to 15° by allowing to stand in a water bath at that temperature, filled up and weighed in the usual way.

*Distillation Test.*—The test to be described is originally due to Engler, certain modifications having been introduced by Ubbelohde. The method is empirical, but gives uniform results if the prescribed dimensions of the apparatus and conditions of distillation are adhered to. If the oil contains much water, it should first be dehydrated by means of calcium chloride, to avoid frothing in the distillation. 100 c.c. of the oil are distilled from a flask of the form and dimensions shown in Fig. 10. A Liebig condenser may be used, and the fractions are collected so that they may be weighed or measured. The distillation should be carried out so that the distillate collects at a uniform rate of two drops per second. At first the flask should be heated on wire gauze, and subsequently a free flame

may be used. The first, or naphtha fraction, is collected until the temperature indicated by the thermometer is 150°; the receiver is then changed for the kerosene

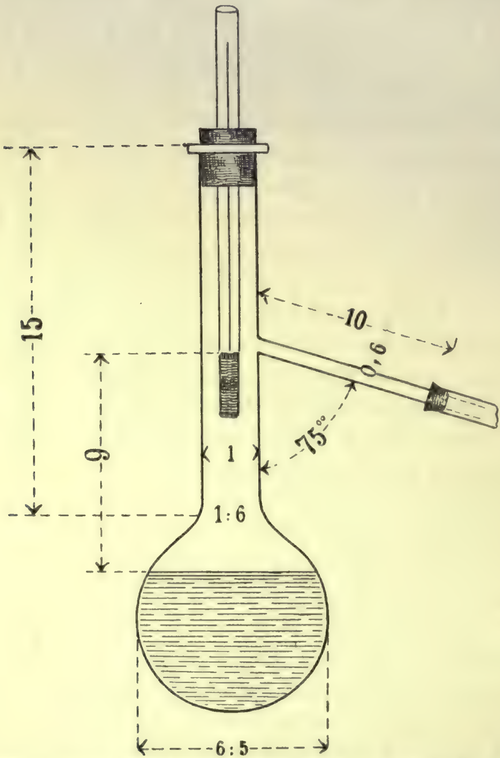


FIG. 10.—Petroleum Distillation Flask according to Engler.

fraction, which is collected between 150° and 300°. In the case of Russian and Galician oils, the kerosene fraction should only be collected up to 285° and 275° respectively, the oils obtained at higher temperatures from these petroleums being unsuitable for burning in

lamps as they cause excessive charring of the wick. What remains in the flask after distilling off the kerosene is weighed as residuum. If desired, separate fractions may be taken at more frequent intervals, say, every 25° ; this is, however, only advisable if the yield of distillate is large. If the oil only yields very little distillate up to 300°, a larger flask, say of 140 c.c. capacity, must be used, or the quantity of oil taken must be reduced to 80 or 90 c.c. ; the heated oil will otherwise expand so as to fill the flask to such an extent that it may be carried over mechanically during the distillation. The same precautions must be taken if the material under examination consists of petroleum residue.

Various petroleums of known origin should be compared by this method. Petroleum is examined for excise purposes in specially constructed metal stills of standard dimensions. For a method of examining petroleum for technical purposes, duplicating the manufacturing operations on a small scale, see Holde's "Untersuchung der Mineralöle und Fette," p. 10.

## The Examination of Petroleum Naphtha and its Distillation Products.

Petroleum naphtha is usually understood to include the portion of the distillate from crude petroleum which comes over below 150° ; on redistillation, however, it is generally found to contain up to 10 per cent. of oils distilling above this temperature.

The various products which are obtained by the fractional distillation of petroleum naphtha are best characterised by their *specific gravity*, which may be determined by means of a float or the Westphal balance which is described in Chapter II., p. 42. The results

may be calculated to 15° C. from the data given in the following table, which is due to Mendeléeff :—

| For Specific Gravities from | | Correction per ° C. |
|---|---|---|
| 0·700 to 0·720 | .. .. | 0·000820 |
| 0·720 ,, 0·740 | .. .. | 0·000818 |
| 0·740 ,, 0·760 | .. .. | 0·000800 |
| 0·760 ,, 0·780 | .. .. | 0·000790 |
| 0·780 ,, 0·800 | .. .. | 0·000780 |

The most important uses of the petroleum naphtha distillates are as fuel in internal combustion engines, and as solvents for extraction of organic material, as, for example, the extraction of fatty oils and fats from seeds and other vegetable products. The requirements for material which is to be used for these purposes are as follows :—

It should be water white and free from objectionable smell ; what smell it possesses should be as faint as possible. An objectionable smell is sometimes masked by the addition of small quantities of turpentine or rosin oil and treatment with alkali ; such additions may be detected as described below. The specific gravities of the better qualities of motor petrol range from 0·710 to 0·720, and of the cheaper qualities from 0·728 to about 0·735 or even higher. When gently heated on the water bath it should leave no oily residue, and when allowed to evaporate on filter paper it should leave no mark. A more accurate test for the presence of heavier oils is the distillation test described below. When agitated with water the latter should remain neutral and give no precipitate with barium chloride solution ; otherwise, the oil will contain some of the sulphuric acid which has been used in the refining process.

The detection and estimation of aromatic hydrocarbons will be described below (p. 136). For the deter-

mination of flash point, which for the present purpose is a test of secondary importance, see the works mentioned in the list at the end of this chapter.

*Fractional Distillation Test.*—The material is distilled in a flask of about 200 c.c. capacity, heated on a sand bath, and fitted with a fractionating column which carries a thermometer and connects with a straight tube water condenser. The test may be carried out as described in Chapter II., p. 43.

According to Holde, the best benzine for motor engines should be completely volatile below 100°, or should, at least, only yield up to 5 per cent. of distillate above this temperature. If it contains a greater percentage of constituents boiling above 100°, it will not evaporate with sufficient rapidity on entering the explosion chamber, especially in cold weather. It is also obvious that benzine which is to be used for extraction purposes must not contain an unduly large proportion of higher boiling constituents, or it will only be removed with difficulty from the extracted material.

*Aromatic Hydrocarbons.*—According to Holde, these may be detected as follows[1]: A small quantity of the benzine is treated with a little powdered asphalt (sufficient to cover the point of a penknife), which has been freed from mineral matter (by solution in benzene and filtration) and repeatedly washed with benzine of specific gravity 0·70 to 0·71 in order to free it from its more soluble constituents. The benzine containing the asphalt is passed through a small filter into a test tube; if the filtrate is colourless, benzene hydrocarbons are absent, if brown, benzene or toluene are probably present.

If a few cubic centimetres of light petroleum containing

[1] Compare also the method for distinguishing petroleum spirit and benzol given in Chapter II., p. 55.

benzene or toluene be shaken in a test tube with a mixture of concentrated nitric and sulphuric acids, the mixture will sooner or later become warm, while the upper layer will develop a yellow coloration; on pouring into water, there will be a separation of yellow, oily drops, having the characteristic odour of nitrobenzene.

The presence of aromatic hydrocarbons will raise the specific gravity of the sample. (See reference in footnote on p. 163.)

The quantitative estimation of aromatic hydrocarbons in benzine may be accomplished by the following method, due to Kraemer and Böttcher, which is based on the fact that the aromatic hydrocarbons (as well as the ethylenes) are absorbed by concentrated sulphuric acid, while the paraffins are unaffected. The acid required is prepared by mixing 80 parts by volume of concentrated sulphuric acid of specific gravity 1·84 with 20 parts of fuming sulphuric acid. 25 c.c. of the benzine (or petroleum) are placed in a strong 75 c.c. flask which has a neck 50 cm. long, graduated in tenths of a cubic centimetre[1]; 25 c.c. of the acid are then added, and the whole is shaken vigorously for 15 minutes. After 30 minutes, acid is filled into the flask until the whole of the upper oily layer comes into the graduated neck, and the volume is read off every hour until no increase in the amount of the indifferent hydrocarbons takes place. The difference between the original volume and the final volume of the oil is the amount of hydrocarbons absorbed by the acid. If more than 13 per cent. of hydrocarbons be absorbed the test is inaccurate.

*Turpentine and Rosin Oils.*—Holde recommends the following test for small quantities of turpentine or rosin

[1] A glass stoppered graduated cylinder may also be employed.

oils, either in pure petroleum benzine or in petroleum benzine containing benzene or homologues of the latter. Bromine vapour is allowed to flow into a test tube containing a little of the benzine ; on shaking the benzine should immediately take up the red colour of the bromine ; if, however, turpentine or rosin oils be present, traces of added bromine will rapidly be absorbed, owing to the unsaturated nature of these substances.

## The Examination of Kerosene or Burning Oil.

Kerosene, or oil for burning in wick lamps, is obtained by redistilling the fraction which succeeds the naphtha fraction in the distillation of crude petroleum. The refining process usually consists in treatment with strong sulphuric acid and subsequent washing with dilute alkali and water, and, where necessary, desulphurisation as indicated above. The specific gravity of American kerosene usually lies between 0·790 and 0·800, and that of Russian kerosene between 0·821 and 0·823, the latter generally being a more homogeneous product than the former. A parallel product obtained from shale oil has a specific gravity of about 0·800. A good kerosene should be water white, or, at the most, of a light yellow colour. Although the degree of colour of burning oil is often made the basis of commercial transactions, this cannot be regarded as giving any real indication as to the degree of refinement or the ability of the oil to burn free from soot and smell and with a steady flame.[1] Burning oils are usually examined colorimetrically by means of Stammer's colorimeter. Instructions for the use of this instrument are supplied by the makers, Messrs. Schmidt and Haensch of Berlin. Various colorimeters will also be found described in the works mentioned at the end of this chapter.

The most important tests to be carried out on burning

[1] Vorschriften der Russischen Regierung nach Einvernehmen mit der kaiserl. Russische Technische Gesellschaft in Baku betr. Nomenklatur und Prüfung von Russischen Erdölproducten.

oils are the distillation test, the specific gravity, the flash point, and the sulphuric acid test for the degree of refinement. Impurities such as sulphur and free acid should also be tested for.

*Distillation Test.*—This test may be carried out with the Engler apparatus, as described above for crude petroleum (p. 159). The temperature of the beginning of the distillation is taken when the first drop of distillate falls from the end of the condenser. Fractions are taken every 50° from 150° to 250°, and then every 25° up to 300°. What remains is estimated by difference. The end point for each fraction is the point at which after cooling at least 20° and reheating to the highest temperature at which the fraction is to be taken, not more than 6 drops of distillate run from the condenser, the process of cooling and heating being repeated till this result is obtained. The volume of each fraction is measured after cooling to the room temperature.

Distillation should not commence below 110°, the yield below 150° should be at most 10 per cent., and the yield above 300° at most 15 per cent. Better class oils yield 85 to 90 per cent. between 150° and 300°, and, at most, 5 per cent. above 300°. The higher the percentage of light oils, the greater the danger of explosion when the oil is burnt in a lamp, while the higher the percentage of high boiling constituents, the more liable will the oil be to clog in the wick and cause charring and uneven burning.

*Specific Gravity.*—The specific gravity of kerosene may be determined by any of the usual methods, as indicated under the heading of petroleum naphtha. The temperature correction per ° C. for reducing results to 15°, as determined by Mendeléeff, varies from 0·000790 for specific gravities between 0·760 and 0·780, to 0·000710 for specific gravities between 0·850 and 0·860. The

specific gravity is mainly used as a test of identity, and is of little use, taken by itself; thus a burning oil might very well contain large proportions both of light and heavy oils and yet show a normal specific gravity; in a case like this, the inferior quality of the oil would only be revealed by the distillation test.

*Flash Point.*—The flash point of burning oils is usually determined in specially constructed "closed testers," which will be found described in the works of reference mentioned at the end of this chapter. The oil is gradually heated while a small flame is brought near its surface from time to time; the temperature at which the oil begins to give off sufficient inflammable vapour to produce a flash is taken as the flash point. The test thus gives an indication of the degree of safety with which the oil may be used in a lamp; the greater the proportion of lighter constituents, as shown by the distillation test, the lower will be the flash point and the greater the danger of explosion. In Great Britain and Canada the Abel tester has been adopted as the standard instrument, the minimum flash points, as laid down by the laws of these countries, being 73° F. and 85° F., respectively. In Germany and Russia, both the Abel and the Pensky-Martens instruments are used, the minimum flash point allowable being 21° C. (70° F.) in Germany, and 28° C. (84·4° F.) in Russia. In the United States various standard instruments and minima have been adopted in different states.

*Degree of Refinement.*—The following method for determining the degree of refinement of burning oils by the colour which they impart to concentrated sulphuric acid has been recommended by the Baku section of the Russian Technical Society. 100 parts by volume of the oil are shaken for 2 minutes in a glass-stoppered cylinder, with 40 parts by volume of sulphuric acid of specific gravity 1·73, at a temperature not exceeding 32°. The acid is then separated off and transferred to a

cylinder of white glass, where it may be compared, as regards colour, with solutions of Bismark brown, of known strengths, contained in similar cylinders. The layers of liquid observed should be of equal depth, and the cylinders should be placed on a uniform white surface. The test solutions are prepared as follows: a solution containing 0·5 gram of the colour per litre is first prepared, and from this ten solutions are made by dilution with water; the first and lightest contains 1 part of the stock solution to 99 parts of water, the second, 2 parts to 98 parts of water, and so on to the tenth and darkest, which contains 10 parts of the stock solution to 90 parts of water. These solutions are numbered from 1 to 10, passing from the lightest to the darkest, and the burning oil is marked according to the solution with which the sulphuric acid extract most nearly corresponds in tint.

As most petroleums are found to come within the limits of 1 to 8, the latter mark is taken to be the maximum limit for a marketable product.

*Impurities.*—Certain petroleums, notably those from Ohio and Canada, contain notable amounts of *sulphur compounds* which it is necessary to remove by special processes of refining, as kerosenes containing more than the slightest traces of such impurities will give a noticeable odour of sulphur dioxide on burning. Owing to the relatively small amounts of sulphur present, even in the worst cases, special methods must be employed for the determination of this constituent. One of the methods most commonly employed is that of Allen, modified by Heussler and Engler, in which a known weight of the petroleum is burnt in a specially constructed lamp, and the products of combustion led over a solution of potassium hypobromite, which is distributed over glass beads. The sulphur is then estimated as sulphate in this solution. The above method is described in most of the works of reference mentioned at the end of this

chapter. According to Holde, a good burning oil should not contain more than 0·02 per cent. of sulphur.

Burning oils should be *free from acid*; about 20 grams of the oil dissolved in a neutral mixture of ether and alcohol containing a little phenol phthalein should show a permanent pink coloration on the addition of one drop of decinormal sodium hydroxide solution.

*Ash* may be determined, according to Holde, by the following method: 500 c.c. or a litre of the burning oil is distilled from a retort until 10 c.c. are left as still residue; the latter is transferred to a platinum dish, by the use of light petroleum, evaporated to dryness, and the residue incinerated.

Good burning oils should, according to Holde, contain not more than 2 milligrams of ash per litre.

## The Examination of Lubricating Oils.

Most of the lubricating oils used nowadays are obtained from the residue which remains after distilling off the naphtha and burning oil from crude petroleum. This residue, which by itself boils above 300°, is distilled in a current of superheated steam at temperatures varying from 180° to 250°, whereby various fractions are obtained which show considerable differences in viscosity and flash point. Deodorisation is effected by blowing with air and treatment with strong sulphuric acid, the latter process being, as usual, followed by washing with caustic soda solution and water. Clarification is effected by filtering over fuller's earth or charcoal. The lighter lubricating oils, which vary in colour from light yellow to brown, and have specific gravities ranging from 0·895 to 0·900, are invariably obtained by distillation; the products of higher specific gravities, up to about 0·940, may consist either of "reduced oils," *i.e.*, filtered residues from which the more volatile portions have been removed by distillation, or of oils which have been distilled *in vacuo* or in a current of superheated

steam. Undistilled products are generally used in the cheaper grades of lubricating oils.

Certain non-drying or semi-drying fatty oils are used as lubricants for delicate machinery, as, for example, neat's foot oil and spermaceti oil, which are used for watches and clocks. Generally, however, when fatty oils are used at all, they are used in admixture with mineral oils. Such blended oils generally contain rape or cotton seed oils which have sometimes been blown with air at elevated temperatures (see Chapter III., p. 95) in order to increase their viscosity. The detection and estimation of fatty oils in presence of mineral oils, and the reasons for their use, will be treated of below. For the present, it may be mentioned that the tendency for fatty oils to undergo hydrolysis and decomposition under the action of steam is greatly reduced when they are mixed with mineral oils. Rosin, rosin oil, coal tar or lignite oils must be considered as adulterants if found in lubricating oils purporting to be of superior grade. The detection of such constituents will be described below.

The requirements of a lubricating oil will naturally vary to a great extent with the conditions under which it is to be used. In general, however, it may be stated that lubricating oils should be free from acids, either mineral or organic, which may cause corrosion of the bearings, and also from all materials which may give rise to the "gumming" of the oil when spread in a thin layer, such as rosin, rosin oil or drying fatty oils. Water or sediment of any kind should be absent.

The function of a lubricating oil is to keep two metallic surfaces from actual contact with one another; for this it is necessary that it should possess a certain "body" or viscosity; the greater the pressure between the surfaces, the greater the viscosity required. On the other hand, the higher the viscosity of the oil, the greater its internal friction; it is, therefore, always advisable to use an oil of the minimum permissible viscosity in order to avoid excessive heating of the bearings. The temperature at which the oil is to be used must also be taken into consideration; thus, the oils employed for the lubrication of

steam cylinders are of a thick and syrupy consistency at the ordinary temperature, as the viscosity invariably decreases with rise of temperature. Fatty oils are sometimes used in cylinder oils, as they lose viscosity with rise in temperature to a lesser degree than do the mineral oils. Oils which are to be used in refrigerating machines, or compressors, are quite mobile at the ordinary temperature, as the viscosity will increase on cooling. The viscosity of a lubricating oil, as determined by means of a viscosimeter, gives an indication of the class of work for which it is best suited, though in this case, practical experience should be the main guide. The Engler and Redwood viscosimeters are the standard instruments adopted for the testing of lubricating oils in Germany and the United Kingdom respectively. The construction and use of these instruments is described in the works mentioned at the end of this chapter. Various machines for testing the lubricating value of oils will also be found described in these works; it is, however, pointed out by Holde that these machines often fail to reproduce the conditions occurring in actual practice.

Other physical properties which must be taken into account are the setting point and the flash point. The determination of these, and their significance in special cases, will be dealt with below.

Lubricating oils are classified by Holde ("Untersuchung der Mineralöle und Fette") as follows:—

(1) *Spindle Oils, for Textile Machinery.* Mobile oils to be used under light pressures; viscosity in Engler degrees at 20° C., 5 to 12; flash point (Pensky), 160° to 200° C.

(2) *Compressor Oils*, or oils for use in refrigerating machines. Mobile oils having low viscosities; Engler degrees at 20° C., 5 to 7. It is important that these oils when submitted to the cold test should remain liquid at − 20°. The flash point may be low (Pensky), 170° to 180°. Compressor oils are often coloured a reddish violet.

(3) *Light Engine Oils*, suitable for motors or dynamos. These are moderately viscous; Engler degrees at 20° C., 13 to 25; flash point (Pensky), 170° to 220°.

(4) *Heavy Engine Oils.* Engler degrees at 20° C., 25 to 45, or in special cases up to 60; flash point (Pensky), 190° to 220°.

The foregoing oils, when viewed in a test tube, are light brownish yellow to brownish red in colour, the more expensive grades being light yellow. The following varieties are dark in colour and often opaque.

(5) *Dark Railroad Oils.* These are classified into summer and winter oils. The former show viscosities of 45° to 60° Engler at 20° C., and the latter 25° to 45°. The flash point (Pensky) should be over 140°. Setting point, for summer oils, under − 5°, for winter oils, under − 20°. (The above requirements for railroad oils are based on the climatic conditions of Germany; in England it is not necessary to prescribe so low a cold test in winter.)

(6) *Cylinder Oils.* These are of a syrupy or sometimes even pasty consistency at the ordinary temperature. The viscosity at 50° C. is 23° to 45° Engler. Oils for superheated steam cylinders have still higher viscosities, *i.e.*, 50° to 60° Engler at 50° C. The flash point should be over 200° and, according to the quality, varies from 220° to 315°; the better qualities flash above 260°. Low volatility is also a desideratum for cylinder oils; this generally follows with a high flash point. Cylinder oils which have been filtered over fuller's earth are of a brownish red colour and transparent; the unfiltered oils are greenish black and opaque.

*Flash Point.*—The determination of flash point by the open test is carried out as follows: about 50 c.c. of the oil to be tested are placed in a porcelain or nickel crucible of about 75 c.c. capacity. The crucible is placed in a tin of convenient size to protect the surface of the oil from draughts, the bottom of which is covered with about half an inch of sand. The tin is heated from below, and the temperature of the oil is indicated by a thermometer, the bulb of which is immersed in the oil without touching the bottom of the crucible. When the

temperature has been raised to about 120°, the oil is tested from time to time by bringing a small gas jet, burning from a hard glass capillary tube, near its surface. The lowest temperature at which the vapour from the oil is observed to ignite is taken as the flash point. When a flash has been obtained, the oil may be cooled about 10° and reheated at the rate of about 2° per minute to get a more accurate determination of the flash point. It should, however, be noted that the flash point will be sensibly raised if the oil is kept too long at an elevated temperature. The results obtained by the open test are not so accurate as those obtained by means of the closed testers, *e.g.*, the Abel or the Pensky-Martens instruments, but for practical purposes, it is only necessary to be able to say whether the oil will be dangerous or not. The flash points indicated by the closed testers are usually about 15° lower than those obtained by the open test.

The determination of flash point is of especial importance in the case of oils which are to be used for textile machinery and oils for lubricating steam cylinders. If the oil has a high flash point, it is not only less liable to damage the india-rubber packings of the cylinders by ignition, but also less liable to loss by evaporation on prolonged exposure to elevated temperatures. The lighter oils for lubricating bearings and journals usually flash between 175° and 200° by the open test. The heavier machine oils should show flash points of 200° and upwards, while cylinder oils of good quality should flash above 280° by the open test. Considerable quantities of fatty oils are sometimes added to mineral cylinder oils of inferior quality in order to counterbalance their tendency to evaporate at the temperature of the steam cylinder, and their low flash points.

*Setting Point.*—The following method for the determination of the setting point of lubricating oils is

recommended by the Scottish Mineral Oil Association. The oil is cooled in a large strong walled test tube until it completely solidifies. In the absence of liquid carbon dioxide or air, the following freezing mixtures may be employed: a mixture of 2 parts of snow or pounded ice with 1 part of sodium chloride, which gives a minimum temperature of $-23°$, or a mixture of 12 parts of snow or pounded ice, 5 parts of sodium chloride and 5 parts of ammonium nitrate, which gives a minimum temperature of $-30°$. When the oil has solidified, the test tube is removed from the freezing mixture and held up to the light, while the oil is stirred with a thermometer; the temperature at which the last trace of paraffin disappears is taken as the setting point. The test is repeated until two determinations give concordant results.

As mentioned above, lubricating oils for refrigerating machines should remain liquid at $-20°$. The setting point, or, as it is sometimes called, the cold test, is also of importance in the case of lubricating oils for machinery which is used in the open in countries where the winter is severe; thus for some winter oils it is necessary to prescribe a setting point of $-15°$ or $-20°$. In England, however, the cold test is of less importance. If the oil should solidify in the journals or bearings, friction would be developed with consequent damage to the machinery.

*Specific Gravity.*—In the case of the lighter oils, a float may be used; for thicker oils, it will be necessary to use a specific gravity bottle, as described for crude petroleum.

The specific gravity has no relation to the lubricating power of an oil, but mainly serves as a means of classification and identification. The specific gravities of pure mineral lubricating oils usually lie between 0·884 and 0·930 at 15°. The specific gravity cannot be looked

on as proportional to the viscosity of the oil, but it may be said that, as a rule, oils of high specific gravities are used for high pressures.

*Water.*—Ordinary lubricating oils should contain no water. In light coloured oils water is easily detected by inspection on shaking the sample; in dark oils it will be revealed by the bumping or spitting which will take place on heating. If desired, any water which may be present may be estimated as described for crude petroleum.

*Acidity.*—The free acids liable to occur in lubricating oils may consist of sulphuric acid which has remained in the oil after the refining process, or organic acids arising from the decomposition of the mineral or vegetable oils. A high acidity may also be due to the presence of rosin or rosin oil, the detection of which will be described below.

Sulphuric acid may easily be detected by shaking out the oil with warm water, and testing the latter when separated, with barium chloride solution and hydrochloric acid; this impurity will, however, only be found in very exceptional cases.

The acidity of lubricating oils may be determined by titration as described under the heading "Acid Value" in Chapter III. If difficulty is experienced owing to the dark colour of an oil, the following process, recommended by Holde, may be employed: 20 c.c. of the oil are shaken in a glass stoppered measuring cylinder with 40 c.c. of neutral absolute alcohol, the oil being warmed if not sufficiently mobile. The cylinder is stoppered and allowed to stand overnight, after which 20 c.c. of the clear alcoholic layer are titrated with decinormal sodium hydroxide solution, using phenol phthalein as indicator. If more than 0·03 per cent. of acid (calculated to $SO_3$) is found, the rest of the alcohol should be poured off, the above process repeated with the

residual oil and a further quantity of 40 c.c. of neutral alcohol, and the amount of acid found in this second titration added to that found in the first.

Refined, clear mineral oils should contain no free acid, or, at most, only 0·03 per cent., calculated as $SO_3$. Dark oils should not contain more than 0·3 per cent. of acids; generally, however, the proportion of these constituents will be under 0·15 per cent. If the amount of free acids in a lubricating oil is above the prescribed limits, there is danger of the bearings on which it is used becoming corroded.

*Soap and Ash.*—The better class lubricating oils will contain no soap or foreign inorganic matter, as will be shown by their complete solubility in benzene. Soap may be added in order to increase the consistency of the oil or to facilitate its emulsification with water; it will be recognised by the ease with which emulsions are formed, and the feebly alkaline reaction of these towards phenol phthalein. An examination of the aqueous extract will soon show whether soap is present (see Chapters III. and IV., introductory sections), and the nature of the base (usually soda potash, lime or ammonia) may be ascertained by examining the acidified aqueous extract. The soap may be estimated as described for lubricating greases.

*Lubricating Greases.*—Soap is chiefly used in lubricating greases, in which it is emulsified with mineral, lignite, rosin or tar oils, with the addition of a little water. The soap may be estimated by carefully burning off a weighed quantity of the sample, incinerating and titrating the residual potassium carbonate, sodium carbonate, or lime, with semi-normal hydrochloric acid. The amount of the base found may then be calculated to stearate or rosinate. (See Chapter IV., p. 128.) If the base present is ammonia, this must be estimated by one of the usual methods in

the aqueous acid extract obtained from a known weight of the sample by extracting it with dilute mineral acid. Water may be estimated in lubricating greases by the xylene distillation method, as described for crude petroleum. The oily portion may be separated for examination for the constituents mentioned above by adding ether, extracting several times with water to remove the soap and then evaporating off the ether. If desired, the aqueous soap solution, which has been entirely freed from oily matter, may be examined as described in Chapter IV.

### Detection and Estimation of Fatty Oils, Rosin, Rosin Oil, Tar Oil, etc., in Presence of Mineral Oils.

*Fatty Oils.*—As a preliminary test, the saponification value of the sample may be determined as described in Chapter III., p. 95. If no definite value is obtained, then fatty oils may be assumed to be absent. The following method for the rapid determination of fatty oils in presence of mineral oils is recommended by Schreiber :—

5 grams of the oil are weighed out in a 200 c.c. conical flask, 25 or 50 c.c. of approximately semi-normal alcoholic potash (see Chapter III., p. 96) are added, and then sufficient benzene to dissolve the oil when warmed. 25 c.c. of benzene will generally be sufficient, but for cylinder oils 50 c.c. may be necessary; in this case, 25 c.c. of neutral alcohol may be added with advantage. At the same time, a blank experiment is started with equal amounts of alcoholic potash, benzene and alcohol, to those used in the actual determination. The flasks are connected with air condensers and placed on a water bath so that the contents are kept gently simmering. During the saponification, which will be complete in

30 minutes, the contents of the flasks should be gently shaken from time to time. The amount of potash used up in the saponification is determined by titration with semi-normal acid in presence of phenol phthalein, as described under the heading "Saponification Value" in Chapter III. For practical purposes, the saponification value of the fatty oils used in lubricating oils may be taken as 195. Then, if S be the saponification value found, the percentage of fatty oil present will be $\frac{100\ S}{195}$.

Some cylinder oils may contain about 30, or even 60 per cent. of fatty oils. The reasons for such additions have already been explained.

*Rosin* (see also Chapter IV.).—As was pointed out above, a somewhat high acidity may be due to the presence of dissolved rosin. In light coloured mineral oils, rosin may be detected by the Liebermann-Storch reaction, as described in Chapter IV., p. 144. If the oil be too dark, the rosin acids may be dissolved out by extracting with dilute sodium hydroxide solution and precipitated by acidifying the alkaline extract. This process may also be adapted for the quantitative estimation of rosin, provided that fatty oils are not present; the precipitated acids are filtered off, dried, weighed, after which they may be tested by the Liebermann-Storch reaction.

A quicker way of separating the rosin for qualitative examination is to shake about 10 c.c. of the oil with an equal volume of hot 70 per cent. alcohol, and after cooling, filtering and evaporating the alcoholic layer. If rosin be present, the residue will be of a resinous nature, and not oily, and it will give the characteristic coloration in the Liebermann-Storch test.

If fatty oils are present, it will be necessary to saponify as described under the heading "Fatty Oils" (p. 177). The alcohol and benzene having been removed by evaporation, the residual soap is dissolved in water, and the solution separated from unsaponifiable matter by extraction with ether. The soap solution is then evaporated to dryness, redissolved in water, and the solution acidified with hydrochloric acid; the precipitated acids are extracted with ether, after which the aqueous layer is separated off, neutralised and evaporated to about 25 c.c. On acidifying again and extracting with ether, the rest of the fatty acids will be separated. The ethereal extracts are united and evaporated; the residue may then be tested for rosin acids by the Liebermann-Storch reaction. If desired, the rosin acids may be estimated by Twitchell's process, as described in Chapter IV., p. 144, in the mixture of fatty and rosin acids obtained, as just described, from a given weight of the oil (sufficient to give about 5 grams of mixed acids). It should be noted that rosin acids which have been treated with hydrochloric acid, as in the Twitchell process, no longer give the Liebermann-Storch reaction.

*Rosin Oil.*—Rosin oil is obtained from rosin, or colophony, by destructive distillation. It always contains varying quantities, up to about 30 per cent., of unchanged rosin acids which have been carried over mechanically in the distillation, and may, therefore, be tested for in lubricating oils, as described above, by the Liebermann-Storch reaction. Rosin oil gives a violet coloration when shaken with a drop of stannic bromide (Allen).

There is no thoroughly satisfactory method for the quantitative estimation of rosin oils in presence of mineral oils, the best methods available being those of

Valenta and Storch, which are based on the solubility of rosin oil in glacial acetic acid and 96 per cent. alcohol, respectively. These, and also other methods for the detection of rosin oils, will be found described in the works mentioned at the end of this chapter.

Rosin oils are generally used in axle greases, together with soap and water, or as insulating material for electrical machines. Owing to their tendency to resinify when exposed to the air in thin layers at elevated temperatures, they are unsuitable for use in the better class lubricating oils. Rosin also has a tendency to cause gumming, and, like rosin oil, must be regarded as an adulterant if found to be present in better class lubricating oils.

Lubricating oils are sometimes tested for their *gumming tendency* by spreading them in thin layers on glass plates and keeping them at 50° or 100° C., the film being examined on cooling, from day to day. If rosin oil be compared in this way with a mineral lubricating oil of good quality, the superiority of the latter as regards gumming tendency may be shown.

*Tar Oils.*—The tar oils which are used for the adulteration of mineral lubricating oils are usually the heavy dark anthracene mother liquor oils (see Chapter II.), of specific gravity over 1·00. If present in fairly large quantity, therefore, they may sometimes be recognised by the somewhat high specific gravity of the sample. According to Holde, the following properties of tar oils enable them to be recognised in presence of mineral oils. They are completely soluble in alcohol at the ordinary temperature, giving dark-coloured solutions, and their smell is generally creosote like. When heated on the water bath with concentrated sulphuric acid, they react to form water soluble products. With nitric acid of specific gravity 1·45, they react vigorously, often with explosive violence, with the formation of nitro compounds.

*Lignite Oils.*—The lignite oils of high boiling point and specific gravity 0·9 to 0·97, which may be used for the adulteration of mineral oils, resemble the coal tar oils in having a creosote like smell; they are soluble in twice their volume of alcohol at the ordinary temperature, to the extent of 22 to 62 per cent. They contain unusually large amounts of sulphur compounds, and react with concentrated nitric acid less vigorously than the coal tar oils, but more vigorously than the mineral oils. They are not so easily recognised in mixtures as the coal tar oils.

The detection of other possible constituents of lubricating oils, such as dissolved rubber, deblooming agents, etc., will be found described in the works mentioned below.

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# CHAPTER VI

## MILK AND BUTTER

### Introductory

On account of the enormous value of the milk of the cow as an article of food, both in its original state and when manufactured into such products as butter or cheese, its complex nature and its susceptibility to decomposition through the agency of the manifold species of micro-organisms for which it forms an excellent nutrient medium, the examination of this product may well be said to form one of the most important and interesting chapters in the chemistry of foods. The examination of whole milk, skim milk, cream, condensed milk and butter will be described below.

Ordinary cow's milk of commerce is a white opaque emulsion of fat in water which contains lactose, saline matter and other substances in solution, and casein in a state of colloidal suspension. Its bluish or yellowish tinge depends on the amount of fat present, or on the presence of colouring matter, either natural or artificial, in the latter.

Fresh milk has an amphoteric reaction, turning blue litmus slightly red, and red litmus slightly blue ; this is owing to the presence of acid phosphates ; on an average, 100 c.c. of fresh milk will be found to require about 30 c.c. of decinormal sodium hydroxide solution for neutralisation in presence of phenol phthalein, and 40 c.c. of decinormal sulphuric acid in presence of litmus as indicator. On standing, milk which has not previously been heated almost invariably becomes decidedly acid owing to the conversion of part of the lactose into lactic acid by certain micro-organisms.

The most important constituents of milk are water,

fat, proteins, lactose and inorganic salts. Roughly, nine-tenths of the weight is water and one-tenth solid matter. The following data, showing the general variations in the composition of cow's milk, have been compiled by Barthel from many different sources :—

| | | |
|---|---|---|
| Specific gravity | 1·029 to 1·034 | |
| Fat | 2·5 „ 4·5 | per cent. |
| Total solids | 10·3 „ 14·7 | „ |
| Solids less fat | 7·8 „ 10·2 | „ |
| Fat in solids | 19·9 „ 32·0 | „ |
| Specific gravity of solids | 1·3 „ 1·4 | „ |

Fleischmann gives the following figures, which are based on numerous analyses :—

| | | |
|---|---|---|
| Water | 86·5 to 89·5 | per cent. |
| Fat | 2·7 „ 4·3 | „ |
| Proteins | 3·0 „ 4·0 | „ |
| Lactose | 3·6 „ 5·5 | „ |
| Ash | 0·6 „ 0·9 | „ |

All the above values are based on analyses of samples of mixed milk from herds of cows ; if based on analyses of samples from individual animals, the variations would have been far greater. The composition of milk varies, not only with the age, state of health, and breed of the animal, but also with the district, climatic conditions, time of the year, general treatment, method of feeding and other factors. It therefore follows that the standard values used for purposes of comparison should be based on as large a number of analyses as possible, while the values adopted as the minimum permissible amounts of fat and solids less fat may vary in different countries.

Before proceeding to describe analytical methods, a short account will be given of the principal constituents of milk and butter.

### The Constituents of Milk.

*Fat.*—As stated above, this constituent is present in the form of an emulsion ; the globules of fat generally measure from 0·0016 to 0·01 mm. in diameter, and

number, on an average, $2\frac{1}{2}$ to 3 millions per cubic millimetre. In milk, the fat is present in the liquid, supercooled state ; on transformation into butter fat, it takes up the solid form which melts from 31° to 36°. This change is effected by thoroughly agitating cream which contains about 25 to 35 per cent. of fat, and which has usually previously been soured or " ripened " by lactic acid producing organisms, in specially constructed churns, at temperatures of about 10° to 15° ; the solid fat coalesces and separates from the buttermilk in the form of small pellets, which, after washing with water, are worked by a process of kneading into butter containing some 12 to 16 per cent. of water. The composition of butter will be further treated of below.

When milk is allowed to stand at rest, the fat rises to the top, forming a layer of milk rich in fat, known as cream. In modern dairy practice, milk is separated in centrifugal machines from which it is possible to obtain cream containing anything up to 80 per cent. of fat at will ; the skim milk obtained contains a few tenths per cent., or even less, of fat.

Milk fat is peculiar in containing an unusually large number of different glycerides which include notable proportions of the glycerides of the lower fatty acids, especially butyric acid. As is pointed out in Chapter III., the latter circumstance is taken advantage of in the estimation of butter fat by the Reichert-Wollny and other processes in which the volatile fatty acids obtained from a given weight of the fat are estimated. Besides the lower fatty acids, milk or butter fat yields on hydrolysis higher fatty acids such as palmitic, stearic and oleic acids (see Chapter III., introductory), the acids of intermediate molecular weight being obtained in relatively small proportion. Milk fat is the most valuable fat known, and is, economically, the most important constituent of milk. The commercial valuation of milk is based very largely on its fat content, while from the fat percentage of the milk yielded by individual cows it is possible to calculate the amount of butter obtainable in relation to the fodder consumed by the animals.

Although the fat in milk from individual cows may

vary from 1 to 8 per cent. when exceptional cases are included, the variations for mixed milk from herds of cows, taken all the year round, usually fall between 2·5 and 4·5 per cent. In order to illustrate the influence of the breed of the animals, it may be mentioned that the milk from Jersey cows averages 5 per cent. of fat, while that from Dutch cows only averages 3·1 to 3·2 per cent. The standards adopted by different countries in fixing the minimum permissible proportion of fat will naturally vary to some extent. In the United Kingdom it is generally presumed that genuine milk should contain at least 3 per cent. of fat, and accordingly the Sale of Milk Regulations of 1901 provide that milk containing less than 3 per cent. of milk fat (or less than 8·5 per cent. of milk solids other than fat) is to be presumed not to be genuine, unless the contrary be proved. Thus, no absolute standard is fixed, but the burden of proof would lie with the defendant in the case of a prosecution.

*Proteins.*—The total proteins of milk amount, on an average, to about 3·5 per cent., of which about 2·9 per cent. is casein, and 0·6 per cent. milk albumin together with traces of milk globulin. Casein belongs to the phosphoproteins, but differs from other phosphorus-containing proteins in that it yields no xanthine and pyrimidine bases, or pentoses, on hydrolysis. Owing to the absence of carbohydrate groupings, it fails to give the Molisch reaction; this test (which may be carried out with egg albumen) consists in adding to an aqueous solution of the protein a few drops of an alcoholic solution of $\alpha$ naphthol and then concentrated sulphuric acid; if carbohydrate groupings are present, as is the case with egg albumen, a violet coloration will be formed at the surface of contact of the acid and aqueous layers.

On hydrolysis with baryta solution, casein yields, besides carbon dioxide and ammonia, a number of amino acids which consist, in the main, of monoamino fatty acids and cyclic derivatives of the latter. Pure casein is a white powder, insoluble in water and soluble in dilute alkali or acid solutions. It thus possesses feebly basic and acidic properties. In milk, casein exists in the form

of a calcium salt, which, being present in the colloidal state, can only be filtered off by passing the milk through a filter of unglazed porcelain; in this way the total proteins of the milk may be obtained as a white mass.

When milk is treated with a small proportion of acetic or mineral acid, or allowed to become sour through the agency of lactic acid producing organisms, it thickens owing to the precipitation of the casein which has been liberated from its calcium derivative. On warming the acidified solution, the casein coagulates, leaving a slightly turbid, yellowish whey, while on addition of excess of acid it is redissolved. On the addition of rennet, tannic acid, alcohol or inorganic salts, such as sodium chloride, copper sulphate, alum, etc., to milk, the casein is precipitated unchanged, in the form of the calcium derivative. In the latter respect, it resembles the majority of proteins, which may usually be separated and purified by the salting out of their aqueous solutions at various definite concentrations and temperatures.

Milk albumin is very similar in composition and properties to the albumin of the blood. It is not precipitated with the casein on the acidification of milk, and further differs from casein in not being salted out from neutral solution on saturation with magnesium or ammonium sulphate. It is, however, precipitated from slightly acid solution on saturation with the above salts.

*Milk Sugar.*—Milk sugar, or lactose, is a disaccharide which, on hydrolysis with dilute mineral acid, yields the hexoses galactose and glucose in equal amounts. It reduces Fehling's solution, and is dextrorotatory in aqueous solution, the hydrated lactose $C_{12}H_{22}O_{11}, H_2O$ having a specific rotation of $[\alpha]_D + 52{\cdot}53°$ at 20° C. As will be shown below, the two last-mentioned properties are made use of in the quantitative estimation of lactose.

The fermentation changes undergone by lactose play an important part both in the preservation of milk and the manufacture of butter from cream. Lactose is not fermented by the common yeasts, most of which attack cane sugar; by far the most important fermentation change which it undergoes is its transformation into lactic acid ($C_{12}H_{22}O_{11} + H_2O = 4\ C_3H_6O_3$).

This change is brought about through the agency of different species of micro-organisms which occur in milk, and is, under normal conditions, the first change in the decomposition of unheated milk by micro-organisms. As was pointed out above, the milk becomes coagulated owing to the precipitation of the casein by the acid. In modern dairy practice, cream is soured for butter-making by first pasteurising it, *i.e.*, heating to about 70° to 85°, in order to destroy most of the micro-organisms present, and then, after cooling to the ordinary temperature, infected with a pure culture of a lactic acid producing organism, such as *Streptococcus Lacticus*. By this means it is possible to obtain more uniform results and a better flavour in the butter than if, as in the old process, the cream were allowed to ripen spontaneously through the agency of such naturally occurring bacteria as may obtain a predominating influence. The formation of lactic acid is, quantitatively, the chief change which occurs in the souring of milk or cream ; at the same time, however, traces of aroma-producing substances are formed which play an important part in the flavouring of the butter fat.

*Mineral Matter.*—The analysis of the ash of milk, allowing for the phosphorus contained in the proteins, and the carbonate formed from the organic matter on incineration, shows the mineral matter of milk to be composed as follows (Söldner, quoted from Barthel) :—

| | Per cent. |
|---|---|
| Sodium chloride .. .. .. | 10·62 |
| Potassium chloride .. .. .. | 9·16 |
| Mono potassium phosphate .. .. | 12·77 |
| Dipotassium phosphate .. .. | 9·22 |
| Potassium citrate .. .. .. | 5·47 |
| Dimagnesium phosphate .. .. | 3·71 |
| Magnesium citrate .. .. .. | 4·05 |
| Dicalcium phosphate .. .. .. | 7·42 |
| Tricalcium phosphate .. .. | 8·90 |
| Calcium citrate .. .. .. | 23·55 |
| Calcium combined with casein .. | 5·13 |
| Total.. .. .. .. | 100·00 |

All the above constituents exist in the dissolved state, with the exception of the calcium combined with the casein, which exists in the colloidal state, and part of the calcium phosphate, which, although existing in the solid form, is exceedingly finely divided.

*Other Constituents.—Lecithin*, a glycero-phosphate of the trimethyl-ammonium base, choline, occurs, on an average, to the extent of about 0·065 per cent. in milk. The presence of this substance is said to cause the "browning" which takes place on heating butter.

*Enzymes* of different kinds are contained in milk; these include oxidases, reductases, catalases, and protein and fat hydrolysing enzymes. The significance of some of these enzymes, some of which are probably produced by the bacteria in the milk, will be dealt with later.

*Dissolved gases*, consisting of oxygen, carbon dioxide, etc.

Among *foreign bodies*, constantly occurring in milk, are white blood corpuscles or leucocytes, bacteria, yeasts, moulds and their spores and dirt.

The number of micro-organisms and amount of dirt contained in new milk depend on the cleanliness of the cows, the stable, and the vessels in which the milk is collected, as well as on the care which is taken in the subsequent treatment of the milk. Thus, while milk from clean cows, collected in steam-sterilised vessels, may contain only a few hundred bacteria per cubic centimetre immediately after milking, milk from dirty cows, collected in dirty vesssels, may contain several hundred thousand bacteria per cubic centimetre. The dirt, which may consist of hairs of animals and human beings, earth, fodder, fibres, sand, parts of insects, etc., may amount to as much as 0·03 to 0·25 per cent. of the milk, but should, in general, be below 0·01 per cent.

## The Constituents of Butter.

As will be gathered from the above remarks on the production of butter, the latter contains the constituents of milk in altered proportions. The percentage of fat in butter will generally lie between 83 and 85 per cent.,

water between 12 and 15 per cent., while the proteins generally amount to about 0·6 to 0·9 per cent., sugar and lactic acid to 0·4 per cent., and ash, *i.e.*, inorganic salts, to 0·1 or 0·2 per cent.

The fat, which differs from milk fat in being in the solid state, is present in the form of minute globules, emulsified in the aqueous serum which holds the proteins, or curd, in suspension and the other constituents, such as inorganic salts and sugar, in solution. The content of curd may vary somewhat according to the method of manufacture of the butter; thus, Storch gives the average protein content of butter from fresh cream as 0·64, and of butter from ripened or soured cream as 0·84 per cent. A certain amount of salt is almost invariably added to butter as a flavouring medium and as a preservative, in order to check the development of micro-organisms which may turn it rancid. The amount of salt added may vary from 1 to 5 per cent., the so-called fresh or mild cured butters containing less than $1\frac{1}{2}$ per cent. Brine-pickled butters may contain as much as 6 to 9 per cent. of salt. Boric acid or borax preservative may be added in amounts up to one half per cent., expressed as boric acid.

## The Physical and Chemical Examination of Milk, Cream and Skim Milk.

*Sampling.*—For a complete examination, exclusive of the estimation of dirt, about 500 c.c. will be required. Owing to the tendency of the fat to collect at the top, the sample should always be taken after thoroughly mixing the bulk of the milk. The sample bottle and cork should be perfectly clean, and sterilised by wrapping in filter paper and heating in an air oven to about 130° to 150° for half an hour. The bottle should not be filled more than about three-quarters full, in order that the cream may be mixed into the bulk of the milk by shaking, immediately before examination.

If the analysis cannot be proceeded with at once, the sample is best preserved by keeping it in a cool place, preferably in an ice chest. The addition of 0·5 gram of potassium dichromate, or 1 c.c. of a 40 per cent. solution of formaldehyde per litre, will preserve milk for a prolonged period; it is, however, advisable to avoid, as far as possible, tampering with the sample in any way; further, the addition of dichromate will naturally affect the specific gravity and content of ash and solids less fat, while the addition of formaldehyde may interfere with the determination of fat by centrifugal methods.

Immediately before the analysis the sample bottle should be repeatedly turned in order to mix the cream with the rest of the milk, heating, if necessary, to about 40°. The milk is then poured into a clean beaker; if any cream remains in the bottle, the milk should be returned to it and shaken until only a trace of cream adheres to the sides. Every time a portion of the sample is to be weighed or measured off, it should be mixed by pouring from one vessel to another. In case the sample for analysis should be soured and coagulated, a special method of treatment is recommended by Weibull, for which see Barthel's "Analysis of Milk and Dairy Products."

## Physical Examination.

The analytical processes described under this heading include the determination of specific gravity and dirt or foreign matter. In appearance, the milk should be fully opaque and homogeneous, and on standing at rest, it should form a well-defined layer of cream; a collection of flaky particles indicates either udder disease or that the milk is so old that bacterial decomposition has set in. Skim milk will, of course, separate no cream layer. A sour taste or smell indicates that lactic acid-producing organisms have become active, while a bitter or saltish

taste indicates either that the milk is derived from cows which have been improperly fed or are suffering from udder disease, or else that the proteins of the milk are being decomposed by bacteria with the formation of peptones. A metallic taste is generally due to the use of untinned vessels, while the use of certain fodders, such as mangel-wurzels or turnips, also produces characteristic tastes in the milk. Milk very easily acquires the taste and smell of materials such as carbolic acid or dung if left in their neighbourhood for some time.

*Specific Gravity*.—The specific gravity of milk is determined with the object of detecting adulteration, either by addition of water or removal of cream; the interpretation of the results will be left to a subsequent section. (See "Solids less Fat.")

FIG. 11.—Soxhlet's Lactometer.

The determination should not be made within a period of 3 hours of the milking, owing to the slight increase in specific gravity which takes place at first, probably owing to some change in the colloidal state of the casein. The determination may be carried out in the usual way by means of the Westphal balance, specific gravity bottle, or, as is more commonly the case, with a float specially designed for the purpose, known as a lactometer. Soxhlet's lactometer is furnished with a thermometer, and is graduated to show specific gravities from 1·024 to 1·038. The length of the scale divisions is so adjusted that the fourth decimal place may be estimated. The instrument is adjusted to 15° C., the specific gravity found indicating the ratio of a given weight of the milk to

that of an equal weight of water at this temperature. Readings may be reduced to 15° by adding two units to the fourth decimal place for each degree above 15°, and subtracting two units for each degree below; these corrections hold good for temperatures between 10° and 20° C.

Before taking the specific gravity the sample should be well mixed and then poured into a cylinder of suitable size, avoiding the formation of froth on the surface. The float is carefully lowered into the milk until the division 1·030 coincides with the surface, and then allowed to come to equilibrium of its own accord. Keeping the eye on a level with the surface of the milk, the reading is taken at the highest point at which the milk is seen to rise up the spindle. The specific gravity of whole milk usually lies between 1·029 and 1·034, or, as is sometimes stated, between 29° and 34°. Skim milk has a somewhat higher specific gravity, usually between 1·035 and 1·037, owing to the absence of fat.

*Dirt and Foreign Matter.*—The following method by which the foreign insoluble matter is estimated in milk is due to Stutzer: the apparatus required consists of a bottle of about a litre capacity, having a tapering neck, connected by means of a wide piece of rubber tube to a strong test tube without a rim. For the purpose an ordinary Rhenish wine bottle may be used. The bottle is charged with a litre of milk, connected with the test tube, and the whole is allowed to stand for 2 hours in an inverted position, so that any sediment will collect in the test tube. The rubber connection is then pinched together with a clip, and the bottle is disconnected; the milk is decanted from the sediment in the test tube, which is washed several times with distilled water acidified with a little hydrochloric acid, in order

to dissolve the calcium phosphate, which is a normal constituent of the milk. The sediment is collected on a Gooch crucible, washed with water until the filtrate is no longer opalescent, then with alcohol and ether, dried at 100° and weighed.

Berch recommends that the milk should be preserved with formalin (see under "Sampling"), in order that it may be allowed to settle for 24 hours. Gerber has devised a modification of the above method by which a number of determinations may be carried out simultaneously. (See Barthel's "Analysis of Milk and Dairy Products.")

Good clean milk should contain only from 5 to 10 milligrams of dirt per litre, though milk of commerce often contains considerably more. The figures obtained by this method should not be taken too literally, as some of the original dirt may have dissolved in the milk, some adheres to the fat globules and is carried to the surface, while a further quantity may dissolve in the alcohol and ether. Generally speaking, however, the method gives a fair idea of the care which has been taken in the treatment of the milk.

A method by which the relative number of micro-organisms may be roughly estimated with a view to forming an opinion as to the care and cleanliness in the previous treatment of the milk is described later.

## Chemical Examination.

Under this heading will be described the determination of the acidity of milk, fat in whole milk, skim milk and cream, proteins, including casein and albumin, lactose and ash in milk, after which the analytical results will be discussed from the point of view of the detection of the adulteration of milk. Finally, tests for the pasteurising and bacterial contents of milk will be dealt with. The examination of milk, as well as butter, for preservatives will be considered in Chapter VIII.

*Acidity.*—As mentioned above, the production of lactic acid from the lactose of the milk is usually the first change produced through the agency of the micro-organisms which normally occur in milk. A determination of the acidity of the sample will, therefore, enable the analyst to form an opinion as to whether it is fresh or not. The acidity of cream is also determined as described below, as a check on the souring process in butter making. As stated above, normal fresh milk has an amphoteric reaction. A decidedly acid reaction towards litmus will show that souring has already commenced, while a decidedly alkaline reaction will indicate that the milk is derived from sick cows, or that it has been diluted with water. Empirical tests for the freshness of milk are the alcohol and the boiling tests, which depend on the precipitation of the casein, *i.e.*, the curdling of the milk which takes place on adding alcohol or boiling, when the milk contains a certain proportion of free acid.

*The alcohol test* is carried out by adding to 10 c.c. of milk an equal volume of 68 per cent. alcohol and shaking well ; fresh milk shows no change, while milk which has 8·5 or more Soxhlet-Henkel degrees of acidity (see below), or milk from animals with diseased udders, shows a more or less distinct coagulation. Milk for infants should not coagulate on addition of twice its volume of 68 per cent. alcohol.

*Coagulation on warming* in a test tube shows that the milk contains upwards of 0·26 per cent. of lactic acid.

The acidity of milk is determined, according to Soxhlet and Henkel, by adding to 50 c.c. of milk, 2 c.c. of a 2 per cent. solution of phenol phthalein and titrating with quarter-normal sodium hydroxide solution till a faint pink colour remains on shaking. The number of cubic centimetres required in the titration gives the acidity of the milk in Soxhlet-Henkel degrees. It is, of course, not necessary to adhere to the above proportions ;

thus it may be found convenient to use a smaller quantity of milk, and weaker standard alkali solution for the titration.

Fresh cow's milk shows, on an average, 3·5° of acidity according to the above method. Milk in which the process of spontaneous souring has been allowed to complete itself will show an acidity of over 15°, while soured cream for butter making should have an acidity of 12° to 16°.

The number of degrees multiplied by 0·0225, gives the weight of lactic acid present in grams.

*Fat.*—Owing to the great importance of the estimation of this constituent, numerous methods have been devised for the purpose. These may be divided into two classes; *i.e.*, those giving scientifically accurate results, and the more rapid processes for dealing with a number of samples at the same time, which give results of sufficient accuracy for all ordinary work.

Belonging to the former class are:—

(1) *Soxhlet's method*, according to which a certain quantity of milk is mixed with certain amounts of potash solution and water-saturated ether, the ether taking up all the fat, the amount of which is estimated by taking the specific gravity of the solution at a certain temperature.

(2) *Wollny's method*, in which the refractive index of the ethereal fat solution is determined instead of the specific gravity as in the previous method.

(3) *Extraction methods*, in which a known quantity of milk is soaked into porous material such as filter paper (Adams), or granular kaolin (Wilson), which is then extracted with ether in a Soxhlet or similar extraction apparatus, the fat thus obtained being weighed after evaporation of the ether.

(4) *The Röse-Gottlieb Method.*—As this is one of the most convenient methods for the determination of fat in whole milk, skim milk or cream, besides being one of the most trustworthy available, it will be described in detail here. In passing, mention may be made of the Werner-Schmidt, and the Liebermann-Székely methods, which resemble the Röse-Gottlieb method in principle.

The determination of fat in whole milk or skim milk is carried out as follows by the Röse-Gottlieb method :—

10 c.c. of milk, measured from a burette (equivalent to 10·27 grams) or about 10 grams by weight of milk, are introduced into a graduated cylinder, about 60 cm. long, $1\frac{1}{2}$ to 2 cm. in diameter, and graduated in half cubic centimetres from 0 to 100 c.c., from bottom to top. 1 c.c. of aqueous ammonia of specific gravity 0·96 is added from a pipette, and then 10 c.c. of 95 per cent. alcohol. A well-fitting cork, which has previously been soaked in water, is inserted into the mouth of the tube, and the contents are gently agitated by repeatedly inverting the tube ; the casein will be dissolved, and a homogeneous liquid will be obtained. 25 c.c. of pure ether are then added, and the contents of the tube mixed as before. Finally, 25 c.c. of petroleum ether, which is completely volatile below 60°, are added, the contents are well mixed, avoiding violent shaking, and allowed to stand at rest for 6 hours, or until the layers have completely separated from one another. The object of the addition of the petroleum ether is to precipitate the greater part of the water held in solution by the ether. All the constituents of the milk, except the fat, remain in the aqueous alcoholic layer ; it now remains to evaporate a definite proportion of the ethereal solution, and weigh the residual fat. In the mouth of the tube is inserted a well-fitting two-holed cork in which are fitted a short tube bent at right angles and projecting only a millimetre or two below the bottom of the cork, and a syphon tube of about 3 to 4 mm. external diameter, bent round sharply so that both limbs are nearly parallel, and of such a length that all the ethereal solution can be drawn off by its means if desired. The syphon is so adjusted that the bottom of its shorter limb comes within exactly

1·5 c.c. of the surface of the ammoniacal alcohol solution, the cork closing the mouth of the graduated tube. The ethereal fat solution is started running by blowing through the short bent tube, and caught in a tared flask of about 100 to 150 c.c. capacity. After again gently blowing through the shorter tube, in order to drive any of the ethereal solution which may remain in the syphon into the flask, the ether and petroleum ether are carefully evaporated off and the residual fat dried at 105° and weighed. If the stated measures of ether and petroleum ether have been added, and loss by evaporation has been avoided, then the 1·5 c.c. of fat solution remaining in the tube will correspond, nearly enough, to 0·27 gram of fat, so that if 10 c.c. of milk were taken, the fat weighed will correspond to exactly 10 grams of milk. If, on the other hand, the measurements given have not been adhered to, then the volume of the solution syphoned off must be noted, together with the total volume of the fat solution, and a calculation made accordingly. In the case of skim milk, this latter mode of procedure must be adopted, or the whole of the fat may be weighed, as described below for the determination of fat in cream by the present method. The fat weighed should be perfectly clear and free from smell of petroleum ether. The drying of the fat should not be unduly prolonged, or gain in weight may take place owing to oxidation through exposure to air at the temperature of the oven.

The above method gives accurate results with whole milk, skim milk and buttermilk, the latter being treated in the same way as skim milk in respect to the measurement of the fat solution. It may also be applied to the determination of fat in cream as follows: 2 to 3 grams of cream, according to the amount of fat present, are weighed out in a small beaker covered with a watch

glass; the bulk of the cream is poured into the graduated cylinder, and the beaker, with its cover, is re-weighed, the amount of cream taken being estimated by difference. After diluting the cream with water to exactly 10 c.c., the procedure is the same as that described for milk, with the exception that as much as possible of the ethereal fat solution is removed without disturbing the ammoniacal alcoholic layer, after which the remaining traces of fat are transferred to the tared flask by shaking out with two successive portions of 50 c.c. of a mixture of ether and petroleum ether in equal parts and syphoning off as before. The whole of the fat present in the cream is thus weighed; this mode of procedure is recommended for dealing with cream, as small quantities of fat are apt to be retained by the ammoniacal alcoholic solution after the first treatment with ether and petroleum ether. In the case of whole milk, skim milk or buttermilk, however, the process first described may safely be adopted.

*Modification of the above Method.*—Eichloff (*Milchwirtschaftliches Centralblatt*, 1910, p. 114) has designed the modified form of apparatus shown in Fig. 12 for carrying out the determination of fat according to the Röse-Gottlieb process. The vase-shaped vessel possesses obvious advantages over the long graduated tube which it is designed to replace, being of such size and weight that it can conveniently be weighed on the balance; the milk or cream may, therefore, be directly weighed out in it. As there are no graduations, the whole of the fat must be weighed; it is, however, only necessary, after the first portion of the fat solution has beeen syphoned off as completely as possible, to wash out the vessel with two successive portions of 25 c.c. of ether, which need not be shaken with the ammoniacal

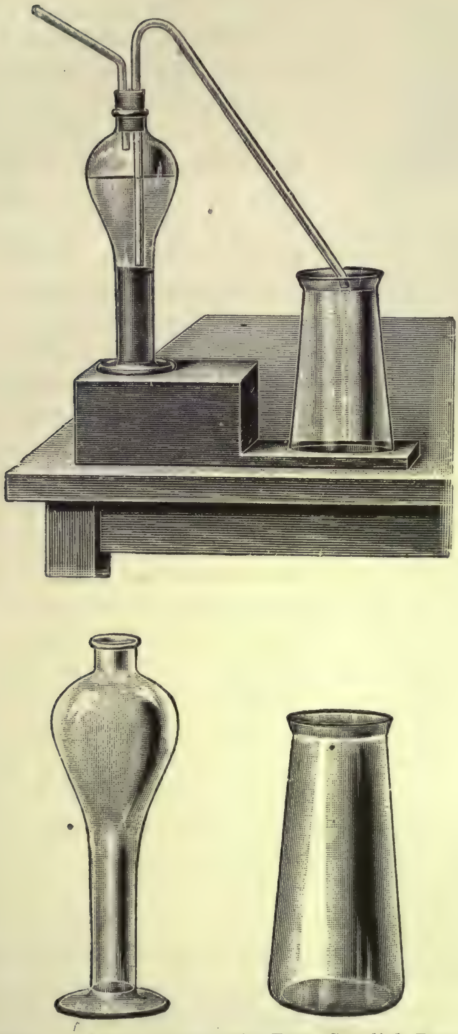

FIG. 12.—Apparatus for the Röse-Gottlieb Process.


FIG. 13.—Butyrometer Tube for determining Fat in Milk.

alcohol. The drying of the fat is considerably facilitated by using the specially designed beaker flask shown in the figure, instead of an ordinary flask. After the solvent has been evaporated off, the fat may be completely dried within 1 hour; in this way, errors owing to oxidation are avoided. With the modifications just mentioned, the process is carried out in the same way as described for the original Röse-Gottlieb process.

*Rapid Methods for the Determination of Fat in Milk and Cream.*—In the methods which are most commonly employed in practice, the fat is separated from the other constituents of the milk or cream by the use of the centrifuge, and its volume read off. As an example, Gerber's method will be outlined.

Fig. 13 shows one form of butyrometer tube which may be used for the analysis of milk by this process. Into this tube are introduced 10 c.c. of concentrated sulphuric acid of specific gravity 1·825 at 15° C., and 11 c.c. of the milk, taken from a well-mixed sample, are carefully run in so as to avoid complete admixture with the acid. Finally, 1 c.c. of amyl alcohol of

specific gravity 0·815 at 15° C. and boiling point between 128° and 130° is added. The acid and alcohol which are employed to facilitate the separation of the fat in a clear layer are generally added from measures which automatically deliver the required amounts. A well-fitting long rubber stopper is inserted in the butyrometer tube, which is then whirled in a centrifuge at about 1,000 revolutions per minute for 3 to 4 minutes. The tube and its contents are brought to 65° in a water bath, and the fat percentage is directly read off by observing the graduation to which the meniscus of the fat layer reaches, the lower surface having been brought to the zero division by manipulating the rubber stopper.

Similar tubes may be obtained for the analysis of skim milk or cream by this method. The tubes for whole milk are usually graduated to show up to 7 or 8 per cent. of fat, while those for cream show up to about 40 or 60 per cent. of fat, using either 5 grams or 5 c.c. of cream. The special tubes, measures, and all other requisites for the above process, may be obtained from most dealers in chemical apparatus.

A large number of determinations may be rapidly carried out by the methods involving centrifuging, the results obtained being sufficiently accurate for ordinary technical and commercial work.

*Proteins.*—The method of estimation of the total proteins of milk by treating 10 grams of milk according to the Kjeldahl process for estimating nitrogen, and calculating the percentage of nitrogen thus found to proteins, by multiplying by 6·37, does not give very reliable results, as the whole of the nitrogen contained in the milk is not present as proteins. Better results are obtained by estimating separately the casein and albumin by the methods now to be described.

*Casein.*—The determination of this constituent must be carried out on fresh or nearly fresh, uncoagulated milk. If the analysis cannot be proceeded with during the next 24 hours, the sample should be preserved as described under the heading of "Sampling," preferably by keeping it in a refrigerator, but failing this, by means of potassium dichromate.

The methods by which casein is separated from albumin and other constituents of milk depend on the fact that the casein is salted out, *i.e.*, precipitated, by the addition of solutions of certain salts such as alum or magnesium sulphate, while the albumin is not so precipitated, excepting in the presence of free acid. After the casein has been salted out the albumin may be precipitated by the addition of tannic acid, with which it forms, like most of the proteins, an insoluble compound; it may also be precipitated from the saturated magnesium sulphate solution by boiling with a little dilute acetic acid. Both the casein and the albumin are estimated as nitrogen by the Kjeldahl process. An alternative method consists in precipitating the casein by adding a little dilute acetic acid to the diluted milk and estimating the albumin in the filtrate by the Kjeldahl process. The latter method is, however, not so reliable as the others indicated above, as the casein is not always quantitatively precipitated by means of acid.

The American Association of Official Agricultural Chemists recommend the following method for the estimation of casein in milk:—

To 5 grams of milk add 50 c.c. of a solution of magnesium sulphate saturated at 45°, and heat the mixture to 45° till the precipitate separates and subsides, leaving the supernatant liquor clear. Collect the precipitate on a filter, wash two or three times with a solu-

tion of magnesium sulphate, as used above, at the same temperature, *i.e.*, 45°, and, after drying in the steam oven, transfer the filter and precipitate to a Kjeldahl digestion flask for the determination of the nitrogen.[1] The amount of nitrogen found, multiplied by 6·25, gives the weight of casein present in the sample analysed.

An alternative method for precipitating casein (Schlossman) is to dilute 10 c.c. of milk with 40 c.c. of water, and to add, while stirring, 1 c.c. of a cold saturated solution of alum, when the casein quickly separates. If the supernatant liquid is not quite clear a further quantity of alum solution, not exceeding 0·5 c.c., is added, drop by drop. The casein is then filtered off and estimated as nitrogen by the Kjeldahl process.

For the precipitation of the casein by means of acid, the following method is recommended by the American Official Association of Agricultural Chemists :—

10 grams of milk contained in a beaker are diluted with 90 c.c. of water at 40° to 42°, and 1·5 c.c. of a 10 per cent. solution of acetic acid in water is added at once. The mixture is stirred with a glass rod and allowed to stand for 5 minutes, after which the supernatant liquid is poured off, and the precipitate washed with cold water by decantation. The casein is collected on a filter and estimated as nitrogen by the Kjeldahl process.

*Albumin.*—The filtrate with washings obtained by any of the above methods, from the precipitated casein, is treated with 10 c.c. of a solution of 4 grams of tannic acid in 8 c.c. of 25 per cent. acetic acid, which has been made up to 200 c.c. with 40 to 50 per cent. alcohol ; the resulting precipitate is filtered off after settling, washed, dried and analysed by the Kjeldahl process. The amount of

[1] For a description of the Kjeldahl process, see Chapter I., p. 22.

nitrogen found, multiplied by 6·34, gives the amount of albumin (and globulin) present in the milk.

It was stated above that albumin is only precipitated from a saturated solution of magnesium sulphate in presence of acid. If the casein has been precipitated by means of this salt, as in the first of the methods described above, the albumin may be precipitated by neutralising the filtrate from the casein with dilute sodium hydroxide solution, adding 0·3 c.c. of 10 per cent. acetic acid and heating in boiling water for 10 to 15 minutes. The precipitate is collected on a filter and analysed for nitrogen, as in the previous method.

It is, of course, necessary that the filter paper used for collecting the precipitated proteins should be either free from nitrogen or else of known nitrogen content, as it is treated together with the proteins in the Kjeldahl determination. The tannic acid used should also be tested to make sure that it is free from nitrogen.

*Milk Sugar.*—Two methods will be described for the determination of this constituent in milk, the one gravimetric and the other optical.

*Gravimetric Method.*—The process to be described, due to Allihn and Soxhlet, depends on the ability of lactose to reduce a warm alkaline solution of a cupric salt (Fehling's solution), the amount of the insoluble cuprous oxide formed under given conditions being taken as a measure of the lactose present. It will be seen that the same principles are involved as in the method for the estimation of cane sugar described in Chapter IV., p. 137, excepting that the lactose reduces the Fehling's solution direct, while the cane sugar itself has no reducing action, but must first be hydrolysed, or inverted, by heating with acid. The amount of lactose corresponding to a given weight of copper or copper oxide, as obtained by the

method to be described, is determined by reference to the accompanying table, as the amount of cuprous oxide precipitated is not strictly proportional to the amount of lactose present. Before the actual estimation of the lactose in milk can be proceeded with, the proteins must be removed as follows (Ritthausen) :—

25 c.c. of milk are weighed out and diluted with 400 c.c. of water in a 500 c.c. flask. The proteins are precipitated by adding 10 c.c. of Fehling's copper solution (containing 69·28 grams of $CuSO_4$, $5H_2O$ per litre, *not* the alkaline tartrate solution), and then sufficient decinormal sodium hydroxide solution to give a neutral or feebly acid

SOXHLET'S TABLE FOR FINDING THE WEIGHT OF LACTOSE CORRESPONDING TO A GIVEN WEIGHT OF COPPER REDUCED ACCORDING TO ALLIHN AND SOXHLET'S METHOD OF DETERMINING LACTOSE.

| Cu, milligrams. | Lactose, milligrams. | Cu, milligrams. | Lactose, milligrams. | Cu, milligrams. | Lactose, milligrams. |
|---|---|---|---|---|---|
| 140 | 101·3 | 240 | 176·9 | 340 | 255·8 |
| 145 | 105·1 | 245 | 180·9 | 345 | 259·8 |
| 150 | 108·8 | 250 | 184·8 | 350 | 263·9 |
| 155 | 112·6 | 255 | 188·7 | 355 | 268·0 |
| 160 | 116·4 | 260 | 192·6 | 360 | 272·1 |
| 165 | 120·2 | 265 | 196·4 | 365 | 276·3 |
| 170 | 123·9 | 270 | 200·3 | 370 | 280·5 |
| 175 | 127·8 | 275 | 204·3 | 375 | 284·8 |
| 180 | 131·6 | 280 | 208·3 | 380 | 289·1 |
| 185 | 135·4 | 285 | 212·3 | 385 | 293·3 |
| 190 | 139·2 | 290 | 216·3 | 390 | 297·7 |
| 195 | 143·1 | 295 | 220·3 | 395 | 302·0 |
| 200 | 146·9 | 300 | 224·4 | 400 | 306·3 |
| 205 | 150·7 | 305 | 228·3 | | |
| 210 | 154·4 | 310 | 232·1 | | |
| 215 | 158·2 | 315 | 236·0 | | |
| 220 | 161·9 | 320 | 239·9 | | |
| 225 | 165·6 | 325 | 243·8 | | |
| 230 | 169·4 | 330 | 247·7 | | |
| 235 | 173·1 | 335 | 251·7 | | |

Factor for converting CuO to Cu = 0·7989.

reaction. Usually, from 6·5 to 7·5 c.c. of the alkali solution will be sufficient; in no case should enough be added to produce an alkaline reaction. 20 c.c. of a cold saturated solution of sodium fluoride are then added in order to remove the dissolved calcium salts, the presence of which tends to influence the results of the sugar determination. After allowing to settle for half an hour the flask is filled to the 500 c.c. graduation, and the clear solution filtered through a dry filter. In a deep porcelain dish, 50 c.c. of Fehling's solution (made by mixing 25 c.c. of the copper sulphate solution, as used previously, with 25 c.c. of a solution containing 250 grams of potassium hydroxide and 350 grams of Rochelle salt per litre) are heated to boiling, and 100 c.c. of the filtrate containing the lactose, obtained as just described, are added. After stirring, the mixture is boiled for exactly 6 minutes, and the precipitate formed is filtered off on a Gooch crucible, washed with water, alcohol and ether, ignited and weighed as CuO, as described on p. 140.

*Polarimetric Method*.—In this method advantage is taken of the optical activity of lactose. A clear whey, containing the lactose, may be prepared for polarimetric examination by the following process, due to Wiley:—

60 c.c. of milk are treated with 10 c.c. of a solution of mercuric nitrate, prepared by dissolving mercury in twice its weight of nitric acid of specific gravity 1·42, and diluting the resulting solution with 4 times its volume of water. The mixture of milk and clearing solution is made up to 100 c.c., filtered through a dry filter and transferred to a 2 or 4 decimetre tube for the determination of optical activity at 17·5° C. The specific rotation of the hydrated lactose, $C_{12}H_{22}O_{11}H_2O$, is $[\alpha]_D + 52{\cdot}5°$. Hence if C be the concentration of the lactose in the solution under observation, expressed in grams per 100 c.c.,

$C = \frac{100 \times D}{52 \cdot 5 \times L}$, where D is the angular rotation observed, and L the length of the tube in decimetres. The volume of the solution, after clearing and making up to 100 c.c., is 100 c.c. minus the volume of the precipitate, containing the fat and proteins, which is allowed for as follows: the weight of fat in grams contained in the milk taken, multiplied by 1·075, and the weight of proteins, multiplied by 0·8, subtracted from 100, gives the volume of the solution in cubic centimetres. The weight of hydrated milk sugar in 60 c.c. of milk is thus found. Dividing by the specific gravity of the milk the weight in 60 grams of milk is arrived at, and further, multiplying by 0·95 will give the weight of anhydrous milk sugar present.

The percentage of anhydrous milk sugar in the milk may thus be calculated by the following formula:—

Percentage of anhydrous lactose

$$= C \times \frac{100 - (1 \cdot 075F + 0 \cdot 8P)}{Q} \times \frac{100 \times 0 \cdot 95}{\text{sp. gr.}},$$

where Q = the number of cubic centimetres of milk taken, F = the weight of fat in the quantity Q, P = the weight of proteins in the quantity Q.

*Total Solids.*—About 20 grams of milk are weighed out in a flat dish, evaporated to dryness on the water bath, and the residue is dried at 105° till constant in weight. In order to prevent the formation of a skin on the surface of the milk a few drops of alcohol or acetic acid may be added; the process of evaporation will thereby be facilitated.

The total solids in milk may also be calculated from the specific gravity, by Fleischmann's formula, as described under the heading of the "Detection of the Adulteration of Milk," where the interpretation of the results of the determination will be discussed. The

last mentioned method is usually employed in practice, on account of its rapidity.

*Ash.*—20 grams of milk are weighed into a platinum dish and evaporated to dryness on the water bath, with the addition of a few drops of acetic acid or alcohol to prevent the formation of a skin. The residue is carbonised at a clear red heat, cooled and extracted with water. The aqueous extract is filtered, taking care that as little as possible of the carbonaceous matter is brought on to the filter. The remaining coal, which has now been freed from most of the mineral matter, is burnt to ash, after which the aqueous extract containing the mineral matter is returned to the dish and evaporated to dryness. The whole is then heated at a low red heat until a perfectly white ash is obtained, cooled and weighed.

The above procedure must be adopted if accurate results are desired. If the total solids are directly incinerated undue loss will occur. As it is, a slight loss will always occur owing to the decomposition of the citrates, loss of water by the mono- and di-phosphates and volatilisation of the chlorides.

If more than 0·75 per cent. of ash is found, the milk is probably abnormal. According to Vieth, the proportion of lactose to proteins, to ash, in normal milk, should be as 13 to 9 to 2. In abnormal milks, the ash is often high and the milk sugar content low. It will easily be understood how such a state may be brought about by the addition of water.

*Other Constituents.*—For the determination of the other constituents of milk, such as citric acid and lecithin, see the works mentioned at the end of this chapter.

### THE DETECTION OF THE ADULTERATION OF MILK.

The most commonly practised methods of adulterating milk are as follow: (1) Addition of water, (2) removal

of cream, (3) simultaneous addition of water and removal of cream. While it is of the greatest importance that such an important foodstuff as milk should reach the consumer in an unadulterated condition, the addition of water is especially to be deprecated on account of the risk attaching thereto of introducing pathogenic germs such as, for example, those of typhus, diphtheria or cholera, all of which are capable of multiplying rapidly in milk.

(1) *Addition of Water. Nitrate Reaction.*—This reaction, which is often prescribed for the detection of added water, is based on the fact that normal milk should contain no nitrates, and on the assumption that most well and tap waters contain small quantities of nitrates. The following test for nitrates is accordingly applied with the object of detecting added water: to 10 c.c. of milk add 1 drop of formaldehyde solution and about 10 c.c. of pure sulphuric acid of specific gravity 1·815. In the presence of nitrates, a bluish violet coloration is developed, which also depends on the presence of milk proteins.

In addition to the fact that all waters do not contain nitrates, it should be noted that the washing out of the tanks and other vessels used for storing the milk with water which contains appreciable quantities of nitrates may give rise to a perceptible nitrate reaction, even though the milk be perfectly genuine. The indications afforded by this test therefore require confirmation by other means, as indicated below.

*Specific Gravity, Fat Percentage and Solids less Fat.*—The tables on p. 183 show the extreme variations in the composition of normal milk from many different sources. The percentage of solids less fat is subject to least variation, and is, therefore, generally used as a basis for the detection of added water, and the calculation of the extent of the adulteration. The addition of water to milk will obviously tend to lower the percentage of solids

less fat, and also the specific gravity and the percentage of fat. As was stated above, in the United Kingdom it is assumed, for purposes of the Sale of Food and Drugs Act, that genuine milk should contain at least 3·0 per cent. of fat, and 8·5 per cent. of solids less fat. Mixed milk, in which the percentage of solids less fat falls below 8·4, is almost certain to have been adulterated by the addition of water, while a specific gravity of 1·028 will render the milk liable to suspicion; a lower value will indicate that adulteration with water is practically certain to have taken place. The specific gravity of milk is lowered by approximately 3°, *i.e.*, 3 places in the third decimal place, for each 10 per cent. of added water.

In order to detect the addition of water to milk and to calculate the probable extent of the adulteration, it is usual to determine the fat percentage and the specific gravity, and from these to calculate the percentage of solids less fat by the use of Fleischmann's formula :—

$$A = 1{\cdot}2 \times F + 2{\cdot}665 \frac{100s - 100}{s}$$

$$\text{and } S = A - F,$$

where A is the percentage of total solids, including the fat, F is the percentage of fat, $s$ the specific gravity of the milk at 15° C., and S the percentage of solids less fat.

This formula was elaborated by Fleischmann from the results of numerous analyses; it depends on the relative constancy in the composition of the solids less fat in normal milks from different sources; naturally, it will only hold good for milks which are normal in this respect, *i.e.*, those in which the proteins, ash and lactose are present approximately in the proportion of 9 to 2 to 13. In general, however, this proportion may be assumed to hold good for fresh milk. Instead of applying the above formula each time the solids less fat are to be determined, it is usual to refer to a table containing data based on this formula. A method for the calculation of the probable extent of the adulteration with water will be given below, after the other methods of adulteration have been discussed.

(2) *Removal of Cream.*—While the direct addition of

water to milk gives rise to, and may be detected by, a lowering of the specific gravity, the removal of cream has the opposite effect, as the fat is the lightest constituent of the milk. The rise produced in the specific gravity is, however, too small to be of any use as an indication of the amount of fat removed, the best method for detecting a fraud of this nature being that which would naturally suggest itself, *i.e.*, the estimation of the fat itself. If the fat falls below 3 per cent., the milk is liable to suspicion, and in a law case it would rest with the supplier to prove that it was genuine. From the fat percentage and the specific gravity, the total solids may be calculated by Fleischmann's formula, as described above; the percentage of fat in solids may then be arrived at by a further simple calculation; if this is found to be under 20·0, then adulteration of the milk, either by simple removal of cream or addition of skim milk, is practically certain to have taken place. Further, if skim milk has been added, the solids less fat will be higher than in the unadulterated milk. To sum up, a sample of milk from which cream has been removed or to which skim milk has been added will show a normal or, perhaps, slightly increased specific gravity and percentage of solids less fat, and a low percentage of fat in solids. On the other hand, the addition of water will be detected by a low specific gravity and percentage of solids less fat; while the percentage of fat in the milk may be lowered perceptibly, the content of fat in solids will not be affected.

(3) *Simultaneous Removal of Cream and Addition of Water or Skim Milk.*—An adulteration of this nature may be carried out in such a way that the specific gravity of the sample remains normal, the lowering which would be occasioned by the addition of water alone being counterbalanced by the rise owing to the abstraction of fat. In any case, however, the fraud will be detected by a lowering in the percentage of fat in the milk, and especially by a low percentage of fat in solids. If water has been added, the percentage of solids less fat in the milk will be lowered. If, on the other hand, skim milk has been added, the latter figure may be slightly raised; in this case the nature of the adulteration will be prac-

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tically identical with that discussed under the previous heading. The percentage of fat in solids will naturally be lowered to a greater extent by the addition of skim milk than by the addition of an equal proportion of water, supposing equal amounts of fat to have been removed in both cases, for, in the first case, not only is fat abstracted, but a further quantity of non-fatty solids is added with the skim milk, while in the second case the fat is simply reduced without appreciable amounts of non-fatty solids being introduced with the water.

The foregoing discussion of the methods for the detection of the adulteration of whole milk may be briefly summarised as follows :—

(1) *Addition of Water.*—Detected by low specific gravity and solids less fat: fat in milk, more or less lowered; fat in solids, normal.

(2) *Removal of Cream or Addition of Skim Milk.*—Detected chiefly by low fat in solids: fat in milk, lowered; specific gravity and solids less fat, normal or slightly raised.

(3) *Simultaneous Removal of Cream and Addition of Water.*—Detected chiefly by low fat in solids and low solids less fat: specific gravity may be normal or lowered; fat in milk, lowered.

*Addition of Water to Skim Milk.*—The adulteration of skim milk with water may be detected, as in the case of whole milk, by the lowering of the solids less fat, the lower limit for which, in the case of skim milk, is generally placed at 9·0.

The methods for approximately calculating the probable extent of the adulteration of milk, as described above, will now be outlined.

(1) *Addition of Water.*—For reasons already stated, the calculation is usually based on the solids less fat. The amount of water added to 100 parts of milk may be calculated from the following equation :—

$$X = \frac{100}{r}(r - r_1),$$

where X is the amount of water added to 100 parts of milk, and $r$ the standard percentage of solids less fat

adopted for comparison. As was mentioned above, the lower limit for the solids less fat in milk is usually placed at 8·5. In order to arrive at the probable extent of the adulteration, most analysts take the standard at 8·9 per cent., thus assuming that the milk was normal in this respect before the water was added; if, however, $r$ is taken at 8·5, a minimum figure for the amount of added water will be obtained. In cases of dispute, the solids less fat are sometimes determined in a sample taken under proper supervision from the same source as the suspected sample, and the value found substituted for $r$ in the above formula. $r_1$ is in all cases the percentage of solids less fat found in the suspected sample.

(2) *Removal of Cream.*—The amount of fat abstracted may be calculated from the following formula:—

$$Y = 100 \frac{f_1 - f_2}{f_1}$$

where Y is the percentage of the original amount of fat removed, $f_1$ is the percentage of fat in the original milk, *i.e.*, the standard value, and $f_2$ the percentage of fat in the suspected sample. $f_1$ may be the percentage of fat in a sample taken under proper supervision from the same source as the suspected sample, or, failing this, $f_1$ should be taken at 3·0, the minimum fixed for the purposes of the Sale of Food and Drugs Act. The probable amount of fat removed will, however, in the majority of cases, be more nearly arrived at by taking $f_1$ at a somewhat higher value, say 3·4.

(3) *Simultaneous Removal of Cream and Addition of Water.*—An approximate idea of the extent of the adulteration may be arrived at by applying the following two formulæ:—

$$X = \frac{r}{r_1}(w_1 - w) \text{ and } Y = 100\left(1 - \frac{f_1 r}{f r_1}\right),$$

where X is the amount of water added to 100 parts of milk, $r$ the percentage of solids less fat taken as the standard value for comparison (see above), $r_1$ the percentage of solids less fat in the suspected sample, $w$ the percentage of water in the original milk (obtained by

subtracting the percentage of total solids, including fat, from 100), $w_1$ the percentage of water in the suspected sample, Y the amount of fat taken from 100 parts of milk, $f$ the percentage of fat in the original milk, and $f_1$ the percentage of fat in the suspected sample. In the absence of a genuine sample from the same source as the suspected sample, for comparison, the total solids for calculation of the amount of water in the original milk should be taken at $3{\cdot}0 + 8{\cdot}5$, *i.e.*, 11·5, though a more probable value would probably be obtained in the majority of cases by placing it at, say, $3{\cdot}5 + 8{\cdot}9$, *i.e.*, 12·4. As was pointed out above, by taking the minimum values for the standard percentages of fat and solids less fat, minimum estimates of the extent of the adulteration will be obtained, thus, to a certain extent, giving the supplier of the suspected sample the benefit of such doubt as may arise from the limitations of the analytical methods available.

## The Heat Sterilising and Pasteurising of Milk.

It is a well-known fact that all micro-organisms are destroyed when exposed to a sufficiently high temperature. On this principle it is possible to improve the keeping powers of milk by temporarily heating it to a suitable temperature. It has been found that milk can only be completely sterilised by heating it for at least half an hour to a temperature of about 120° by means of steam under pressure; under this treatment, however, it undergoes such a change in taste as to render it useless as food, and in practice it has been found convenient to employ lower temperatures, at which only a slight "cooked" flavour is produced in the milk. It was shown by Pasteur that temperatures lower than 100° could be employed with success in destroying most of the micro-organisms of milk, and Weigmann has shown that momentary heating to 85° is sufficient to destroy the most resistant of the pathogenic bacteria which are likely to occur in milk. Some bacteria, yeasts and moulds, however, produce highly resistant spores which are only destroyed by a somewhat more prolonged

heating at higher temperatures, and consequently survive the pasteurising process in which the milk is heated to temperatures ranging from about 70° to 85°, either momentarily, or, at most, for a few minutes. The heating is carried out either in glass vessels immersed in a water bath at the desired temperature, or in specially constructed continuously working pasteurising appliances. After heating, the milk is quickly cooled, in order to check, as far as possible, the development and growth of the surviving organisms, and preserved so as to avoid infection from the air or other sources.

Pasteurised milk will generally keep unchanged some 24 to 26 hours longer than unpasteurised milk, while sterilised milk will keep for much longer, often for months, without any change being noticeable, provided, of course, that it is preserved so that risk of infection from outside sources is avoided. It should, however, be noted that if pasteurised milk is kept too long, the changes which it will undergo, owing to the action of micro-organisms, will have much more serious consequences than in the case of unpasteurised milk. The reasons for this are as follows: in ordinary milk, kept at the ordinary temperature, the relatively harmless lactic acid producing bacteria develop at a far more rapid rate than all the other types of organisms present, and thus effectively keep the latter in check. In this first stage of decomposition, the milk is protected against putrefactive decomposition leading to the production of poisonous substances, while some time will always elapse before sufficient free lactic acid has been produced to coagulate the milk; even when this has occurred, however, the milk will not contain any poisonous substances resulting from the souring process, and cannot be said to be unfit for food. The lactic acid produced effectively checks the development of the protein hydrolysing, putrefactive bacteria which only become active in neutral or feebly alkaline media, and it is only after the souring process has come to an end (*i.e.*, when the milk contains about 0·8 per cent. of lactic acid), and the lactic acid has been consumed by the yeasts or moulds which usually follow after the lactic acid producing organisms

have ceased to develop, that the putrefactive organisms are able to develop and act on the milk.

When the milk has been pasteurised, the conditions are entirely altered; the lactic acid organisms are destroyed and leave no spores which might survive the elevated temperature. Many putrefactive organisms (*e.g.*, *B. subtilis*, or the hay bacillus), on the other hand, form highly resisting spores which survive the pasteurising process and, on cooling, are able to develop in the absence of lactic acid bacteria. The first stage in the decomposition of pasteurised milk is, therefore, usually due to the development of putrefactive organisms which hydrolyse the proteins of the milk into the bitter poisonous peptones, and further into polypeptides and amino acids. In spite of what has just been said, however, pasteurising has proved to be a useful method of preserving milk, and should certainly be insisted on when the milk is suspected to have been derived from contaminated sources. In modern dairies, where milk from many different sources is mixed for skimming, pasteurising forms a regular feature in the process of butter and margarine making.

The effect of pasteurising on milk may be readily shown as follows: Two clean flasks of about 200 c.c. capacity are plugged at the mouth with cotton-wool, and sterilised by heating to about 140° in an air oven, for about 20 minutes. They are then allowed to cool, without removing the cotton-wool plugs, and nearly filled with fresh milk, the plugs being replaced as soon as possible after the introduction of the milk. One of the flasks is heated in boiling water for about 20 minutes, and then cooled in running water. The two flasks are allowed to stand together at a temperature of about 20° to 25°, and the contents examined from time to time; within about 24 hours, the unheated milk should have acquired a sour taste and smell, and should sooner or later become coagulated; the unheated milk, on the

other hand, should remain unchanged for a much longer time, not developing acidity, and differing only from new milk in having a slightly "cooked" flavour. After the unheated milk has become coagulated, the acidity of the two samples may be compared by titrating a small portion of each with standard sodium hydroxide solution, using phenol phthalein as indicator. On further standing, however, it will be found that a bitter peptone-like taste and smell of decay will develop in the heated sample quicker than in the unheated sample.

*Test for Pasteurising.* (*a*) *Milk and Cream.*—In cases where pasteurising is obligatory, it is desirable to have some means of ascertaining whether the milk or cream for butter making has been sufficiently heated. A test commonly employed is that devised by Storch. Unheated milk decomposes hydrogen peroxide with the formation of oxygen and water, the active substance presumably being an enzyme present in the milk to which the name "catalase" has been given. When the milk has been heated to 80°, it will be found to have lost the power of decomposing hydrogen peroxide, owing to the destruction of the catalytic substance during the heating.

The test is carried out as follows: To 5 c.c. of the sample in a test tube add 1 drop of a 2 per cent. aqueous solution of hydrogen peroxide, shake, then add 2 drops of a 2 per cent. aqueous solution of paraphenylene diamine, and mix again by shaking. If the milk has not been heated, the nascent oxygen from the hydrogen peroxide will act on the paraphenylene diamine, giving rise to a blue coloration within a few seconds. If the milk has been heated above 80°, no colour will be developed in 30 seconds, while if it has only been heated to 79° to 80° a greyish blue colour

will form in about 30 seconds. This test may easily be verified with heated and unheated milk.

(*b*) *Butter*.—The test just described may also be applied to butter, with a view to ascertaining whether it has been made from properly pasteurised cream.

25 grams of the butter are melted in a small beaker at a temperature not above 60°. When the fat has separated clear from the aqueous layer, it is syphoned off. The aqueous serum, which is turbid and contains a white sediment of casein, is diluted with an equal bulk of water, poured into a test tube and tested with hydrogen peroxide and paraphenylene diamine solutions, as directed above.

### The Bacterial Contents of Milk.

*Reductase Test*.—The test which is now to be described affords a means of ascertaining the relative number of micro-organisms present in milk. It has already been pointed out that the alteration in flavour, and decomposition of milk, are due to the action of the numerous species of micro-organisms which grow and reproduce in it. It is obvious that the greater the number of micro-organisms present, the quicker will be the decomposition of the milk. Milk as it leaves the udder of a healthy cow contains relatively few organisms, all of which are generally of a harmless nature. From this moment onwards, however, it is liable to become infected by organisms from the air, or any dirt, fodder, straw, etc., with which it may come into contact. Unless, therefore, the greatest care and cleanliness be observed in the treatment of the milk, its keeping powers will be materially reduced.

The reductase test depends on the ability of milk to reduce methylene blue to a colourless substance; the reduction is not a function of the milk itself, but of the micro-organisms which it contains, or rather of enzymes produced by the latter. The greater the number of

micro-organisms present the shorter will be the time required for the reduction and decolorisation of a given quantity of methylene blue by a given volume of milk.

The test may be carried out as follows: 40 c.c. of milk are introduced into a test tube of about 50 c.c. capacity which has been carefully cleaned and then sterilised by heating to 140° for about 20 minutes. 1 c.c. of a 0·35 per cent. solution of pure methylene blue in water is then added and well mixed with the milk. The tube is immersed in a water bath which is kept between 38° and 40°, and the time taken for the blue colour to entirely disappear is noted. The milk should not be shaken while the reduction is proceeding, or the blue colour may be partially restored owing to atmospheric oxidation; this source of error may be guarded against by covering the surface with a thin layer of paraffin oil. If the time taken for reduction is from 8 to 20 hours, the sample is fresh and clean, if under 5 hours, the sample is old or unduly contaminated with micro-organisms, and if under 1 hour, the sample is either very old, or it has been very carelessly treated as regards cleanliness. This test may be applied simultaneously to a number of samples, the necessary appliances, including an automatic measure for the methylene blue solution, tubes, stands for the latter and water bath, being obtainable from dealers in milk testing apparatus. If, however, only a few tests are to be carried out, the necessary appliances may easily be improvised from the ordinary laboratory equipment. It will be found instructive to compare samples of new and old milk by this test.

*Fermenting Test.*—This test, which may be carried on concurrently with the reductase test (Orla Jensen), has been designed with a view to ascertaining the nature of the principal bacterial contents of the milk. The prin-

ciple involved is as follows: If milk is allowed to stand at 38° to 40°, the development of the micro-organisms which it contains is hastened, with the result that the struggle for existence between the various types of organisms at a temperature approximating that of the alimentary canal will be shown in a relatively short time by the appearance and smell of the milk. In carrying out the test, the milk is filled into tubes similar to those used in the reductase test, described above, and the tubes placed in a water bath which is kept at 38° to 40°. After 12 hours, the samples are examined; in the case of normal, fresh milk, a sour taste and smell will have been developed, and in most cases the coagulum will be perfectly even and homogeneous, showing that the relatively harmless lactic acid producing bacteria outnumber the other types of organisms which may occur in milk, and are able to hold them in check for the time being. If the sample is unevenly coagulated, showing separated whey, the lactic acid producing organisms have not been able to check the development of the protein hydrolysing bacteria, as will be evidenced by a disagreeable smell suggesting putrefactive decomposition. If the proteins have been entirely dissolved, with the production of a slightly turbid whey, then the putrefactive bacteria will practically have obtained the upper hand from the start; this may be taken as a sign that the milk has certainly not been treated with sufficient care as regards cleanliness; in this case also, the whey will have an unpleasant smell, and will probably contain bubbles of gas. A copious evolution of gas, accompanied by a frothy coagulum and a smell of butyric acid, indicates that butyric acid producing organisms have obtained the upper hand; this must also be looked on as a very bad sign.

Both the reductase and fermenting tests should be carried out with a number of samples of fresh and stale milk, in order that the various types of fermentation may be observed; the same samples may be used for both tests, as the addition of the methylene blue does not affect the results of the fermenting test. Further, pasteurised and unpasteurised milk may be compared by the fermenting test. From what has been said on the subject of pasteurising, it is obvious that pasteurised milk should produce a more or less flocculent or uneven coagulum, and develop a bad smell.

## Condensed Milk.

Condensed milk is manufactured by evaporating fresh milk *in vacuo* at temperatures of about 40° to 50° to a quarter or a third of its original bulk. Cane sugar is often added as a preservative to prevent the development of micro-organisms, so that the product may keep indefinitely in closed vessels. If cane sugar is not added, it is necessary to sterilise the condensed milk after tinning. When condensed milk is diluted with 3 to 4 times its bulk of water, it gives a product which has the same composition and general properties as new milk, excepting for the presence of cane sugar which is usually added in sufficient quantity to produce a decidedly sweet taste.

## Analysis of Condensed Milk.

Before taking the sample for analysis, the contents of the tin should be well mixed by stirring. After diluting in accordance with the instructions on the tin, the determination of the various constituents may, in some cases, be proceeded with as in the case of ordinary milk, and the results calculated back to percentages on the original condensed milk; in the presence of cane or invert sugar, special methods, to be described below,

must be adopted for the estimation of the carbohydrates. An unsugared product may be diluted to a specific gravity of 1·032 at 15° in the case of whole milk, or to 1·036 in the case of skim milk. If cane or invert sugar be present, the specific gravity can neither be used as an index for diluting the condensed milk to a strength corresponding to that of ordinary milk, nor for the calculation of the solids less fat as described above.

In the following table will be found typical analyses of different varieties of condensed whole and skim milk, by Buttenberg and others (quoted from W. Grimmer) :—

| — | With Cane Sugar. | Without Cane Sugar. | | Condensed Skim Milk. | |
|---|---|---|---|---|---|
| | | Evaporated to One-Half. | Evaporated to One-Third. | With Cane Sugar. | Without Cane Sugar. |
| Water . . . | 27·88 | 76·70 | 66·91 | 27·43 | 69·0 |
| Fat . . . | 9·62 | 6·80 | 9·75 | 0·29 | 0·30 |
| Proteins . . | 10·27 | 5·89 | 8·95 | 11·59 | 12·4 |
| Lactose . . | 14·20 | 9·13 | 12·50 | 13·60 | 15·7 |
| Cane sugar . . | 36·06 | — | — | 44·92 | — |
| Ash . . . | 1·97 | 1·48 | 1·89 | 2·17 | 2·6 |

*Carbohydrates*.—Besides lactose and cane sugar, or sucrose, it is possible that the condensed milk may contain invert sugar, *i.e.*, the mixture of glucose and fructose obtained by the hydrolysis of sucrose.

The lactose is estimated in the diluted sample as described above for ordinary milk. As has already been mentioned, sucrose does not itself reduce Fehling's solution, and its presence will therefore not affect the determination of the lactose by the gravimetric method. Invert sugar, on the other hand, reduces Fehling's solution, and will, if present, be determined together with the lactose, in which case it will be necessary to determine the latter separately by another method which will be described below.

The total sugar content may be approximately estimated by subtracting the sum of the fat, proteins and ash, determined in the diluted sample, as described above for ordinary milk, from the total solids, determined directly by evaporation, also as described above. Subtracting the percentage of lactose from that of the total sugar, the content of sucrose will be found with sufficient accuracy for most purposes. If greater accuracy is desired, the sucrose must be determined separately, as described below.

If the amount of reducing sugar found would correspond to a larger proportion of lactose relatively to the proteins and ash in the sample than would be expected in ordinary milk, then the presence of invert sugar may be suspected. If, on the other hand, the amount of reducing sugar found corresponds with a normal amount of lactose in proportion to the proteins and ash in the sample, but is appreciably less in amount than the total sugar, then sucrose may be assumed to be present.

*Qualitative Test for Sucrose.*—Quantities of not less than 1 per cent. of sucrose in condensed milk may be detected by the following method, due to Seliwanoff, and modified by Carlsson: 10 c.c. of milk (or 0·5 gram of lactose to be tested for sucrose, dissolved in 10 c.c. of water) are warmed in a test tube with 50 milligrams of resorcin and 0·5 c.c. of 25 per cent. hydrochloric acid. The presence of sucrose is indicated by a red coloration after boiling for a few minutes, no colour being developed if lactose alone is present.

*Determination of Sucrose.*—The method to be described, which has been elaborated by Stokes and Bodmer, depends on the fact that sucrose may be hydrolysed, or inverted, by a dilute solution of citric acid while the lactose is unaffected. The principles involved have already been explained in Chapter IV., p. 137. Before inversion, the reducing action on Fehling's solution will be due to the lactose alone, or to the lactose and invert sugar, if the latter be present in the original sample; after

inversion, an increased action on Fehling's solution will be obtained, owing to the invert sugar which has been produced from the sucrose, which itself is non-reducing. The increase in the amount of copper oxide obtained after inversion may be converted to sucrose on referring to the table on p. 141. The reason for adopting the following modified method of inversion is that lactose, being a disaccharide, may be partially hydrolysed to galactose, the reducing power of which differs from that of the original lactose, if the ordinary method, involving the use of hydrochloric acid, be employed.

25 c.c. of the diluted condensed milk are treated at the ordinary temperature, with sufficient of a 1 per cent. solution of citric acid to cause coagulation, and made up to 200 c.c. The volume of the precipitated casein, including the fat, is then calculated (this may be done with sufficient accuracy by the method described under the Polarimetric Determination of Lactose in ordinary Milk, on p. 207), and an equal volume of water added, so that the volume of the liquid itself is now 200 c.c. The liquid is passed through a dry filter, and the reducing power of 50 c.c. is determined, as described in Chapter IV., p. 137. A further 50 c.c. of the filtrate is treated with 0·5 gram of citric acid, the latter being dissolved, boiled for fully 30 minutes, and the reducing power determined as before. The directions as to the volume of the solutions, method of heating, etc., given on p. 140, must be strictly followed in both cases.

An alternative method for the determination of sucrose in presence of lactose consists in inverting the former by means of invertase, an enzyme present in ordinary yeast, any action due to the yeast itself or other micro-organisms being avoided by the addition of a little thymol as a preservative. In this process, also, the lactose is unaffected. The method is described fully in Leffman and Beam's "Food Analysis," and other works.

*Determination of Lactose in Presence of Invert Sugar.*—As explained above, if invert sugar be present, the lactose cannot be determined in the ordinary way, by means of Fehling's solution, as the invert sugar also reduces. In the following method, due to Bigelow and McElroy, the invert sugar, and also any sucrose which may be present, is fermented by yeast to alcohol and carbon dioxide; the lactose, which is unaffected by the yeast, may then be estimated by means of Fehling's solution or the polarimeter.

250 grams of the condensed milk are diluted with water, heated to boiling, cooled to 80° and treated with a solution of 4 grams of glacial phosphoric acid in a few c.c. of water. After being kept at 80° for a few minutes, the mixture is cooled, made up to 1,000 c.c., shaken and filtered; the volume of the precipitated proteins, including the fat, is then estimated; this may be arrived at with sufficient accuracy by the method described under the Polarimetric Determination of Lactose in ordinary Milk, on p. 207. Sodium hydroxide solution is added till the solution is all but neutral, and then sufficient water to make up, together with the alkaline solution just added, for the volume of the solids. For the purposes of calculation, the total volume of the liquid may then be taken as 1,000 c.c. After filtering again, the solution is measured in portions of 100 c.c. into 200 c.c. measuring flasks. A solution of 20 milligrams of potassium fluoride in 2 or 3 c.c. of water and 1 gram of compressed brewers' yeast is added to each flask, and the mixtures allowed to stand for 10 days at a temperature between 25° and 30°. The invert and cane sugars will then be fermented and destroyed by the yeast in presence of the fluoride, while the milk sugar remains unaffected. The latter may then be determined in the solutions, either by the gravimetric or by the

optical method, as described under the Determination of Lactose in ordinary Milk. Before proceeding with the actual determination by either method, the contents of the flasks should be clarified by the addition of portions of about 2 c.c. of alumina cream, prepared as described below, made up to 200 c.c., and filtered through dry filters. For the determination by Fehling's solution, a convenient quantity of the filtrate may be taken (10 or 25 c.c.), so that about 150 to 400 milligrams of copper, or a corresponding amount of copper oxide, will be weighed.

*Alumina Cream.*—This is prepared as follows: A cold saturated solution of alum is divided into two unequal parts, and a slight excess of ammonia is added to the larger portion. The remainder of the alum is added in sufficient quantity to give a faintly acid reaction.

Having determined the lactose, it is possible to find the amount of invert sugar present by subtracting the lactose from the total reducing sugar, *i.e.*, lactose plus invert sugar, by a simple calculation; the amount of copper oxide corresponding to the lactose present in the sample taken for the determination of the total reducing sugar is calculated by referring to the table on p. 205, and this is subtracted from the actual amount of copper oxide found in the latter determination. The balance of the copper oxide is due to the reducing action of the invert sugar alone, the amount of the latter being found by referring to the table on p. 141.

*Calculation of the Composition of the Original Milk, and the Degree of Concentration of the Condensed Milk.*—The fat contained in the original milk before evaporation may be approximately calculated from the non-fatty solids in the condensed milk, exclusive of cane sugar, invert sugar, or other added material. For the purposes of the calculation, the percentage of non-fatty solids in ordinary milk may be assumed to be 8·9.

Then, the percentage of fat in the original milk =

$$\frac{\text{Fat in condensed milk} \times 8{\cdot}9}{\text{Solids less fat in condensed milk}}.$$

Or, on the basis of the protein content of the condensed milk, assuming the protein content of ordinary milk to be 3·4 per cent., the percentage of fat in the original milk =

$$\frac{\text{Fat in condensed milk} \times 3{\cdot}4}{\text{Proteins in condensed milk}}$$

In this way it is possible to determine whether the condensed milk has been made from whole milk, or milk which has been deprived of its fat, either wholly or in part. The degree of concentration of the condensed milk may be arrived at by a simple calculation from the solids less fat or proteins contained therein, assuming the percentages of these constituents in the original milk to have been 8·9 and 3·4 respectively.

### THE ANALYSIS OF BUTTER AND MARGARINE.

The composition of butter has already been dealt with at the beginning of this chapter. As a rule, the only essential difference between butter and margarine lies in the composition of the fat. The same methods as are employed for the determination of water, fat, proteins and non-fatty solids in butter may therefore be applied to margarine.

*Sampling.*—In order to obtain a fair average sample of butter from a large mass, a sampling iron, such as is shown in Fig. 14, is generally used. Two or three cylindrical samples are taken in different directions with the iron, introduced into a wide-mouthed glass-stoppered bottle, melted at a temperature not above 40°, and shaken vigorously until solidified; samples for analysis may then be taken from the bottle as required. The butter should not be kept too long before analysis, as it is liable to alter in composition on the development of rancidity.

*Water.*—The estimation of water in butter and margarine has already been described in Chapter III., p. 85.

*Fat.*—The fat in butter or margarine may be determined by the Röse-Gottlieb method, as described for cream, on p. 197. About 2 grams of the sample are weighed out on a piece of fat-free paper, and introduced into the graduated cylinder. After adding sufficient hot water to make up the volume to 10 c.c., and completely melting the sample by immersing the cylinder in hot water, 1 c.c. of the ammonia solution and 10 c.c. of 95 per cent. alcohol are added. When the whole has cooled to the ordinary temperature, 25 c.c. of ether are added, the contents are shaken, 25 c.c. of petroleum ether are added, the contents shaken again and allowed to stand until separated into two well-defined layers. The procedure is the same as that described above for the determination of fat in cream, the total fat being removed and weighed by extracting several times with the mixture of ether and petroleum ether.

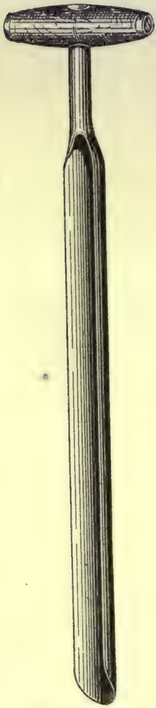

FIG. 14.—Sampling Iron.

Instead of directly determining the fat by the above method or other methods involving extraction with organic solvents, the water and non-fatty solids, including added salt or other preservative, may be subtracted from 100, the balance being taken as fat.

In Germany, the minimum percentage of fat in saleable butter is fixed by law at 80, and the maximum water percentage at 18 for unsalted, and 16 for salted

butter. In the United Kingdom, no definite minimum fat percentage has been laid down by the law, but, as mentioned above, the maximum water percentage is fixed at 16. (See Chapter III., p. 85.)

*Non-Fatty Solids.*—These include casein, or curd, and small amounts of lactose, lactic acid and inorganic salts derived from the milk or cream, as well as any added salt or boric acid preservative.

Barthel, in his "Methods of Analysis of Milk and Dairy Products," recommends the following method for their determination :—

5 to 10 grams of butter (or 10 to 15 grams of unsalted butter) are weighed out in a small beaker or glass dish furnished with a spout, melted at a gentle heat, and treated with petroleum ether.[1] The fat solution is poured off through a tared filter, care being taken that all of the aqueous portion remains in the beaker or dish. A further quantity of petroleum ether is then added and carefully decanted off through the filter, as before. The greater part of the fat will now have been removed from the water and non-fatty solids ; it is recommended that the latter be not entirely freed from fat at this stage, or they will be difficult to remove from the glass vessel after drying. The non-fatty solids are dried by placing the glass vessel in which they are contained in an oven, kept at 100°, for 2 hours. They are then completely transferred to the tared filter by means of petroleum ether, and washed with the latter solvent until free from fat, a drop of the filtrate leaving no grease spot when evaporated on filter paper. The filter containing the non-fatty solids is then dried and weighed. Instead of an ordinary filter, a Gooch crucible in connection with a filter pump may be used with advantage.

*Proteins.*—The proteins are determined by means of

[1] Ether cannot be used for this purpose, as it invariably dissolves some of the salt.

the Kjeldahl process, which is described in Chapter I., p. 22, the amount of nitrogen found being multiplied by 6·37. The determination cannot be conveniently carried out on the butter itself; the non-fatty solids obtained from about 15 grams of butter, as described above, generally being used for this purpose; the filter paper, which should be free from nitrogen, or of known nitrogen content, containing the non-fatty solids, may be transferred direct to the Kjeldahl digestion flask, and treated in the usual way.

*Ash, Salt and Boric Acid Preservative.*—The non-fatty solids, obtained as described above, are ignited in a platinum dish or crucible, with the filter, or on the Gooch crucible, till all the organic matter has been burnt off, and the residue, free from carbon, is weighed. The ignited residue is then dissolved in distilled water, made up to a definite volume, filtered, if necessary, through a dry filter, and the salt determined in an aliquot portion (about half of the total) by titration with decinormal or twentieth normal silver nitrate solution, using potassium chromate as indicator, as is described in most text-books on quantitative inorganic analysis. The boric acid may be determined in butter or margarine by titration with sodium hydroxide solution in presence of glycerol, as described in Chapter VIII., p. 287.

Subtracting the salt and boric acid (if any) from the total ignited residue, the balance should be the ash derived from the natural mineral constituents of the butter. If these do not fall within about 0·2 per cent. of the butter, the latter may possibly contain other added mineral matter.

Methods for detecting other preservatives in butter and margarine will be described in Chapter VIII.

*Examination of the Fat.*—The examination of butter fat has already been dealt with in Chapter III., pp. 119

*et seq.*, where the problem of distinguishing margarine fats from butter fat, and the detection of the former in the latter, has received attention. As a rule, the only important distinction between butter and margarine lies in the composition of the fat.

*Pasteurising Test.*—A test by which it is possible to ascertain whether the cream from which the butter was made has been properly pasteurised is given on p. 217.

*Colouring Matter.*—Small amounts of colouring matter are added to margarine, and also to butter, in order that it may resemble the grass butter of the summer months, all the year round. The vegetable dyes turmeric and anatto, as well as certain azo-dyes, are employed for this purpose; these are harmless, and added in very small amounts. Various methods by which they may be detected and identified, if desired, are given in the works mentioned below.

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# CHAPTER VII

## STARCH AND ITS DECOMPOSITION PRODUCTS—FLOUR, BARLEY AND MALT

### INTRODUCTORY.

STARCH is one of the most important and characteristic products of the vegetable kingdom, not only on account of the prominent *rôle* which it plays in plant physiology, but also on account of its great economic value as a food material for animals and human beings. A considerable portion of the non-nitrogenous reserve food material of plants is, in many cases, stored in the form of starch. The most abundant supplies of this substance are to be found in seeds, tubers, etc., where it remains as such until it can be assimilated by the embryo plant. Starch is one of the most important constituents of the flours used in making bread and many other common articles of food, of rice, which practically forms the staple diet of one-third of the human race, of sago, of tapioca, maize and barley, and of such vegetables as potatoes, beans and peas. As a food starch is used together with the nitrogenous, fatty, saline and other matter with which it is associated in nature.

Starch which has been separated from the other constituents of the grain, usually by washing with water and levigation, is used, as such, for laundry purposes, as a thickening material in calico printing, and for the preparation of adhesive paste.

As regards indirect uses, starch is of importance as a source of alcohol, which results from the action of yeast on the sugar produced from the starch through the hydrolysing action of mineral acids, the enzyme diastase, or certain moulds. In the manufacture of beer, most of the starch contained in the malt is partially hydrolysed

by the action of diastase (an enzyme or mixture of enzymes occurring in barley and other seeds) to dextrin and carbohydrates of a similar nature, only part of the starch being converted into sugar which can be fermented to alcohol by the action of yeast. In the manufacture of alcohol and spirits, on the other hand, the starch is practically completely converted into alcohol, as indicated above. The nature of the chemical changes undergone by starch in the manufacture of beer and spirits will be more fully described when the analytical processes applicable to starch and malt are dealt with.

The starches from maize, wheat, rice and the potato are usually employed for the direct applications; barley is used in the manufacture of beer, whiskey and other spirits, while dextrin and starch sugar, for brewing purposes or conversion into alcohol, are generally prepared from starch from the potato or from damaged or inferior rice, maize, etc.

### Properties and Identification of Starch.

Starch exists in plant cells in the form of well-defined granules, varying in diameter from 0·002 to 0·185 mm. When viewed under a microscope of fairly low magnifying power (about 150 to 300 diameters) the granules show a very characteristic structure, consisting of a hilum, or nucleus, surrounded by a number of concentric rings. In order to show up these peculiarities in structure, which vary to a certain extent with starches from different sources, a small quantity of the powdered starch should be mounted in a dense medium, such as glycerine or chloral hydrate, and viewed, if possible, under oblique illumination. With practice, it is often possible to determine the source of a starch from the shape of the granules and the relation of the concentric rings to the hilum. Further, on examination under a polarising microscope with crossed Nicol prisms, many starches display characteristic arrangements of dark bands, usually giving the appearance of a Maltese cross. If a selenite plate be placed between the lower polarising Nicol prism and the object, colours will be shown with many starches.

The microscopic identification of starches from different sources will not be exhaustively treated of here; the student wishing to pursue the matter further should consult Allen's "Commercial Organic Analysis," Wynter Blyth's "Foods, their Composition and Analysis," or the other works mentioned at the end of this chapter. Starch in general may, however, easily be identified by a simple microscopic examination, though it should be noted that starch which has been treated with water, or exposed to a high temperature, as in bread making, will have lost its characteristic structure, owing to the disruption of the granules. If necessary, colouring matter may, according to Allen, be removed in most cases by extraction with cold water and alcohol.

Starch may readily be identified by the characteristic blue colour which it gives with iodine. This reaction is best carried out by adding to a solution of the starch a dilute solution of iodine in potassium iodide solution, drop by drop; or, if the starch is being observed under the microscope, a drop of the iodine solution may be placed at the side of the cover slip, so that it will gradually diffuse into the glycerine in which the granules are mounted, when the latter will be seen to take up a dark blue colour.

Chemically considered, starch is not a definite substance, but consists of a mixture of two carbohydrates, granulose and starch cellulose, or rather, a series of substances which may be looked on as gradations between the two.

Starch cellulose is a body intermediate as regards complexity of structure, stability and other properties, between granulose and ordinary cellulose; from the latter it differs in being convertible into soluble starch by boiling in water or digesting in caustic alkali solution. It is insoluble in cold water and saliva, and gives a yellow colour with iodine. Granulose, on the other hand, is soluble in saliva, and gives the characteristic blue colour with iodine. Ordinary starch is insoluble in cold water;

on heating with water, however, the granules begin to swell as the temperature approaches 60°, and on further heating they become disintegrated and mix with the water, giving a solution which gelatinises strongly on cooling, and from which starch may be precipitated on the addition of alcohol. The starch thus obtained is soluble in cold water, and is usually known under the name of soluble starch. The soluble variety is also produced when starch is heated in closed vessels to 100°.

Considered as a member of the carbohydrate group, starch ranks after cellulose in point of complexity, stability towards hydrolysing agents, and solubility; when acted on by ordinary diastase, it is converted, first into dextrin, or rather a series of bodies known collectively as the dextrins, and ultimately into dextrin and the reducing disaccharide maltose.[1] Boiling dilute mineral acids convert starch into dextrins, maltose, and finally into *d* glucose, or, as it is commonly called, dextrose. The mechanism of these hydrolyses and the nature of the products formed will be further discussed when the methods for estimating starch are explained.

## Methods for Estimating Starch in Commercial Starches, Flours, Potatoes, Barley, Malt, etc.

The following methods have been chosen with a view to illustrating the nature of the decompositions undergone by starch under the influence of various hydrolysing agents. They include (1) the hydrochloric acid method, in which the starch is converted to glucose, and estimated as such; (2) the diastase method, in which the starch is determined as dextrin and maltose; (3) the combined diastase and yeast method, in which the starch is estimated as alcohol.

(1) *Hydrochloric Acid Method.*—This method, which is prescribed by the American Association of Official Agricultural Chemists (A.O.A.C.), depends on the fact that starch is completely converted into dextrose on boiling with dilute hydrochloric acid. The dextrose

[1] The Author is informed by Mr. W. A. Davis that if Taka diastase is used dextrose and maltose are rapidly formed.

formed may be estimated by means of Fehling's solution, the polarimeter, or even roughly by the specific gravity of its solution, and furnishes a measure of the starch present in the sample. It should be noted that a certain class of gummy bodies known as the pentosans, which are often present in notable proportions in flours, give rise to reducing sugars, *i.e.*, the pentoses (sugars containing 5 carbon atoms in the molecule), on boiling with acids. The method is therefore only applicable to commercial starches which have been freed from extraneous gummy matter, such as, for example, the starches used for stiffening textiles.

3 grams of the sample are mixed with about 50 c.c. of cold water, stirring at intervals for about an hour. The insoluble residue is then collected on a filter and washed with water until the filtrate measures 250 c.c. The residue, which has now been freed from soluble carbohydrates, is heated on a water bath for 2½ hours with a mixture of 200 c.c. of water and 20 c.c. of hydrochloric acid of specific gravity 1·125 (*i.e.*, 2·5 per cent. HCl), in a flask fitted with a reflux condenser. The mixture is then cooled, neutralised with sodium carbonate, made up to 250 c.c., and filtered through a dry filter. The dextrose is determined in an aliquot portion of the filtrate by means of Fehling's solution, as described in Chapter IV., p. 141. The weight of dextrose found, multiplied by 0·9, gives the weight of the starch. This method gives results 3 to 5 per cent. too low, owing to destruction of some of the dextrose by the hydrochloric acid.

(2) *Diastase Method.*—In this method the starch is freed, as far as possible, from extraneous matter, and hydrolysed by means of the enzyme diastase to dextrin and maltose, both of which are then estimated. The advantage over the foregoing method lies in the circumstance that the pentosans and other gum-like products which are converted into reducing sugars by hydro-

chloric acid are not affected by diastase; it may be applied to the estimation of starch in flours, grain, potatoes, malt, etc.

Before giving the working details, a few words must be said regarding the rationale of the process. The hydrolysing action of ordinary diastase on starch proceeds with fair rapidity until four-fifths of the starch molecule have been converted into maltose, and one-fifth into dextrin, the resulting mixture being composed of 80·8 per cent. of maltose and 19·2 per cent. of dextrin. After this stage has been reached the action slows down to such an extent that it is advantageous to stop it altogether, and proceed with the determination of the maltose and dextrin, which will give a measure of the amount of starch originally present.

The changes which take place may be represented by the following equations (A. J. Brown's "Laboratory Studies for Brewing Students"):—

$$1.\ \underset{\text{Soluble starch.}}{5\,(C_{12}H_{20}O_{10})} + 3\,H_2O = \underset{\text{Free maltose.}}{2\,C_{12}H_{22}O_{11}} + \underset{\text{Malto-dextrin.}}{\begin{pmatrix} C_{12}H_{22}O_{11} \\ C_{12}H_{20}O_{10} \end{pmatrix}}$$

$$+ \underset{\text{Stable dextrin.}}{C_{12}H_{20}O_{10}}.$$

$$2.\ \underset{\text{Malto-dextrin.}}{\begin{pmatrix} C_{12}H_{22}O_{11} \\ C_{12}H_{20}O_{10} \end{pmatrix}} + H_2O = \underset{\text{Free maltose.}}{2\,C_{12}H_{22}O_{11}}.$$

The final result of the conversion may thus be represented by—

$$\underset{\text{Maltose.}}{4\,C_{12}H_{22}O_{11}} + \underset{\text{Stable dextrin.}}{C_{12}H_{20}O_{10}}.$$

It will be noticed that the malto-dextrin molecule, represented as being built up of maltose and dextrin molecules, is completely converted into maltose, whereas free dextrin, here referred to as stable dextrin to distinguish it from malto-dextrin, is unaffected under the conditions of the experiment.

Regarding the products of the conversion, maltose, being a typical reducing sugar, may be estimated by means of Fehling's solution. Dextrin, when pure, is an

amorphous white solid, soluble in cold water and possessing an optical activity of $[\alpha]_D = 202 \cdot 0°$. It has no action on Fehling's solution, so that an estimation of the reducing power of the product of the starch conversion, together with its optical activity, will give the amounts of maltose and dextrin present by a simple calculation. Maltose may be separated from dextrin by treatment with alcohol, in which the former is soluble and the latter insoluble.

The method described is due to C. O'Sullivan (*J.C.S.*, 1884, p. 2). Before dealing with the actual determination, two preliminary operations must be described: (*a*) preparation of diastase or malt extract, and (*b*) preparation of the sample.

(*a*) *Preparation of Diastase or Malt Extract.*—Either diastase or malt extract, prepared as directed below, may be used for effecting the hydrolysis of the starch.

(i.) *Diastase.*—2 to 3 kilos. (or a smaller quantity if desired) of finely ground barley malt are steeped in water, just sufficient to cover the whole. After standing for several hours, the mash is filtered by pressing through calico, and the filtrate, if turbid, is passed through an ordinary filter. The diastase is now precipitated from the clear filtrate by adding alcohol of specific gravity 0·83, so long as the precipitate produced is flocculent, the addition being discontinued as soon as the liquid begins to appear milky or opalescent. The diastase is filtered off and washed with alcohol of specific gravity 0·86 to 0·88, dehydrated by further washing with a little absolute alcohol, and dried over sulphuric acid in a desiccator. Diastase thus prepared is a friable, white soluble powder which retains its activity as a hydrolysing agent for starch, for a considerable time.

Diastase is one of the enzymes which convert the starch present in the seed into soluble carbohydrates

which may be assimilated by the embryo plant during germination; the part which it plays in brewing, in converting starch into maltose and products belonging to the dextrin group, will be referred to later.

(ii.) *Malt Extract.*—100 grams of pale malt are digested with 250 c.c. of water at 65°, and allowed to stand at the room temperature for 12 hours. After filtering, the liquid is ready for use.

It is advisable to determine the diastatic capacity of the diastase or malt extract used in the starch determination, by the methods given below (see p. 249), in order to make sure that a preparation of sufficient diastatic activity is being used.

(*b*) *Preparation of the Sample.*—The material, representing a fair average sample, must be freed from extraneous matter by treating it with various solvents which will not act on the starch.

5 grams of the flour, or finely ground malt or barley, are soaked with alcohol of specific gravity 0·82, and 20 to 30 c.c. of ether are added. The flask containing the mixture is corked and set aside for a few hours, after which the whole is filtered, and the residue washed with ether. This treatment will remove fatty matter from the sample.

The next step is to remove matter soluble in dilute alcohol, which includes sugars, albuminoids other than casein, and other substances.

The fat-free flour is transferred to a flask and treated with 80 to 90 c.c. of alcohol of specific gravity 0·90 at 35° to 38° for a few hours, shaking occasionally. The alcoholic solution is passed through the same filter as was used for the alcohol-ether operation just described, and the insoluble residue is washed on the filter with alcohol of the same strength and at the same temperature as already used in the present operation.

Finally, the water soluble material must be removed; this includes, among other substances, the amylans, a group of carbohydrates having the same empirical formula as starch, but differing from the latter in being soluble in cold water, and giving no coloration with iodine. Wheat, for example, generally contains about 2 to 2·5 per cent. of $\beta$ amylan.

The residue from the last operation is digested with 500 c.c. of water at the ordinary temperature for 24 hours, and then decanted through the filter used previously; the insoluble residue is transferred to the filter by means of water, and repeatedly washed with water at 35° to 38°; the latter process may sometimes be very tedious.

(*c*) *Conversion of the Starch.*—The insoluble residue from the last operation is transferred to a beaker, and boiled with 40 to 45 c.c. of water for a few minutes, with constant stirring, in order to convert the starch into the soluble form. The mixture is then cooled to 62° to 63°, and 0·2 to 0·4 gram of active diastase dissolved in a few c.c. of water, or 10 c.c. of an active malt extract, prepared as described above, are added.

If malt extract is used a certain amount of sugar and dextrin will be introduced; this must be determined by making a blank experiment with an equal quantity of the same malt extract, treating this in exactly the same manner as the starch solution, *i.e.*, diluting to the same volume and keeping it at the same temperature for the same length of time. The amount of sugar and dextrin due to the malt extract added to the starch may then be estimated and deducted.

After the addition of the diastase solution or malt extract, the mixture is kept at 62° to 63° in a water bath; in a short time, it will be found that the characteristic

blue coloration will no longer be obtained when a drop of the mixture is treated with a drop of dilute iodine solution; at this point, all the starch will have been converted into maltose and dextrin; it is, however, recommended to continue the digestion for another hour, in order that the subsequent filtration may be facilitated. The contents of the beaker are now boiled for 8 to 10 minutes in order to render the diastase inactive,[1] transferred to a filter, and the filtrate received in a 100 c.c. measuring flask; the residue is carefully washed with small quantities of water at a time, the washings also being received in the measuring flask; when the latter is nearly full, the contents are cooled to 15·5° and made up to 100 c.c. with water at that temperature. Should the volume of the filtrate exceed 100 c.c., it may be concentrated by evaporation. The specific gravity, optical activity and reducing power of the solution are now determined in order to find the amounts of maltose and dextrin present.

(*d*) *Specific Gravity.*—The object of this determination is to find the amount of solid matter contained in the solution; this should, if the above processes have been properly carried out, be found to be very nearly equal to the sum of the maltose and dextrin as determined by the optical activity and reducing power of the solution, together with the added diastase. The specific gravity method is very commonly employed in determining the amount of solid matter contained in solutions of carbohydrates, in preference to the method of evaporating and weighing the residue, owing to the manner in which these bodies retain water. The specific gravity is determined in the usual way by means of a picnometer

[1] Compare the destruction of the hydrogen peroxide decomposing enzyme in milk by heating to 80° (see p. 217).

or specific gravity bottle, and for the purposes of the calculation, expressed as the weight of 1,000 c.c. of the solution in grams. The difference between the specific gravity thus expressed, and 1,000, divided by the number of grams per 100 c.c., gives what is known as the solution factor for the given material.

$$\text{Thus} \quad \frac{\text{Sp. gr.} - 1{,}000}{\text{Gms. per 100 c.c.}} = \text{solution factor.}$$

Knowing the solution factor, the concentration of the solution may easily be calculated from the specific gravity. The solution factors of the various carbohydrates vary slightly with the concentrations of their solutions. They have been determined for solutions of various carbohydrates of varying strengths by Brown, Morris and Millar (*J. C. S.*, 1897, Vol. lxxi., p. 72).

For the purpose of the present estimation, the solution factor to be used is 3·95.

(*e*) *Determination of the Maltose.*—This is carried out according to the method of Brown, Morris and Millar, as described on p. 137.

As maltose is a reducing sugar, hydrolysis is not necessary as in the case of cane sugar. If the directions are adhered to, the amount of maltose present may be calculated from the amount of copper oxide formed, by referring to the accompanying table on p. 243. Dextrin has no effect on Fehling's solution, so that the total copper oxide weighed will be due to the action of maltose.

(*f*) *Optical Activity of the Solution.*—The optical activity of the solution of the starch conversion product is determined in the usual manner, the concentration having been determined by the specific gravity. At the concentrations dealt with, the optical activity of dextrin is $[\alpha]_D = + 200{\cdot}4^\circ$ and that of maltose $[\alpha]_D = + 138^\circ$. Knowing the amount of maltose

TABLE FOR CALCULATING THE AMOUNTS OF MALTOSE CORRESPONDING TO VARYING AMOUNTS OF COPPER.
(Method of Brown, Morris and Millar.)

| Maltose, grams. | Cu, grams. | Maltose, grams. | Cu, grams. |
|---|---|---|---|
| ·070 | ·0772 | ·185 | ·2017 |
| ·075 | ·0826 | ·190 | ·2072 |
| ·080 | ·0880 | ·195 | ·2126 |
| ·085 | ·0934 | ·200 | ·2180 |
| ·090 | ·0988 | ·205 | ·2234 |
| ·095 | ·1042 | ·210 | ·2288 |
| ·100 | ·1097 | ·215 | ·2342 |
| ·105 | ·1151 | ·220 | ·2397 |
| ·110 | ·1205 | ·225 | ·2451 |
| ·115 | ·1259 | ·230 | ·2505 |
| ·120 | ·1313 | ·235 | ·2559 |
| ·125 | ·1367 | ·240 | ·2613 |
| ·130 | ·1422 | ·245 | ·2667 |
| ·135 | ·1476 | ·250 | ·2722 |
| ·140 | ·1530 | ·255 | ·2776 |
| ·145 | ·1584 | ·260 | ·2830 |
| ·150 | ·1634 | ·265 | ·2884 |
| ·155 | ·1692 | ·270 | ·2938 |
| ·160 | ·1747 | ·275 | ·2992 |
| ·165 | ·1801 | ·280 | ·3047 |
| ·170 | ·1855 | ·285 | ·3101 |
| ·175 | ·1909 | ·290 | ·3155 |
| ·180 | ·1963 | ·295 | ·3209 |
| | | ·300 | ·3264 |
| | | ·305 | ·3318 |

Factor for converting CuO to Cu = 0·7989.

present from the reducing power of the solution, the optical activity due to this constituent may be calculated

and deducted from the total optical activity, the difference being due to the dextrin.

The total starch is equal to :—

$$\text{Dextrin} + \text{Maltose} \times 0{\cdot}95.$$

As mentioned above, the maltose and dextrin due to added malt extract must be determined in a blank experiment and allowed for.

(3) *Determination of Starch as Alcohol.* — Although the stable dextrin which is formed as one of the products of the action of diastase on starch in the process just described is only acted on by diastase with extreme slowness, and is not fermented by yeast alone, yet by the joint action of diastase and yeast it is readily converted into alcohol. Maltose, on the other hand, is fermented to alcohol by yeast in the absence of diastase. In the manufacture of alcohol, spirits or vinegar, where the object is to obtain a maximum yield of alcohol from the starch, yeast is allowed to act on the product of the diastatic conversion without destroying the diastase In brewing, on the other hand, where the object is to prepare a product containing dextrin-like products and other carbohydrates, with only a relatively small proportion of alcohol, the diastatic fermentation is arranged so that only a small proportion of maltose is produced, after which the diastase is destroyed by heating, and the product treated with yeast ; in this way the maltose only is converted into alcohol.

In the analytical method under consideration, which has been devised for the estimation of starch in barley, 5 grams of the finely ground sample are extracted, first with alcohol and ether, and then with alcohol of specific gravity 0·90, as described above under the Preparation of the Sample in the Diastase Method for estimating Starch. The residue is washed into a flask with water, and thoroughly boiled in order to remove all traces of alcohol and to gelatinise the starch. The diastatic

conversion is effected by means of diastase or malt extract at 62°, as described above; then, without destroying the diastase by boiling, the conversion product is cooled to 26° to 27°, and submitted to the action of 1 gram of brewers' yeast in a flask at that temperature for several days. The alcohol may then be estimated in the product by the following method, which is very commonly employed for the estimation of alcohol in the presence of non-volatile matter:—

The carbon dioxide is first removed by repeatedly pouring the liquid from one vessel to another, or by filtration, and the whole is made up to 100 c.c., or, if necessary, to a larger definite volume, with distilled water. 100 c.c. are then distilled from a flask of convenient size connected with a straight tube condenser, until 80 c.c. of distillate have been collected. The distillate is made up to 100 c.c. with distilled water, and its specific gravity determined at 60° F. by means of the picnometer or specific gravity bottle.[1] Reference to the accompanying tables will show the percentage of alcohol in the distillate. In order to calculate the percentage of absolute alcohol in the sample before distillation, it will be necessary to know either its specific gravity and volume or its weight, and likewise, also, the specific gravity and volume or the weight of the distillate.

Then

$$\frac{\text{Sp. gr. of distillate} \times \text{vol. of dist. in c.c.} \times \text{\% of alcohol in dist.}}{\text{Sp. gr. of sample} \times \text{vol. of sample in c.c.}}$$

= Percentage of absolute alcohol by weight contained in the sample, or

$$\frac{\text{Weight of dist.} \times \text{\% of alcohol in dist.}}{\text{Weight of sample taken.}}$$

[1] For a description of the exact determination of specific gravities of liquids, see Allen's "Commercial Analysis," Vol. I., pp. 5 & 6, 1909 edition.

TABLES (ABRIDGED) ADOPTED BY THE AMERICAN ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

PERCENTAGE OF ALCOHOL AND SPECIFIC GRAVITY.

FOR MIXTURES OF ALCOHOL AND WATER.

(Recalculated from the determinations of Gilpin, Drinkwater and Squibb, by E. Richards.)

| Specific Gravity at $\frac{60°}{60°}$ F. | Per cent. Alcohol by Volume. | Per cent. Alcohol by Weight. | Specific Gravity at $\frac{60°}{60°}$ F. | Per cent. Alcohol by Volume. | Per cent. Alcohol by Weight. | Specific Gravity at $\frac{60°}{60°}$ F. | Per cent. Alcohol by Volume. | Per cent. Alcohol by Weight. | Specific Gravity at $\frac{60°}{60°}$ F. | Per cent. Alcohol by Volume. | Per cent. Alcohol by Weight. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1·00000 | 0·00 | 0·00 | 0·99629 | 2·50 | 1·99 | 0·99281 | 5·00 | 4·00 | 0·98959 | 7·50 | 6·02 |
| 0·99923 | 0·50 | 0·40 | 0·99557 | 3·00 | 2·39 | 0·99215 | 5·50 | 4·40 | 0·98897 | 8·00 | 6·42 |
| 0·99849 | 1·00 | 0·79 | 0·99487 | 3·50 | 2·80 | 0·99149 | 6·00 | 4·80 | 0·98837 | 8·50 | 6·83 |
| 0·99775 | 1·50 | 1·19 | 0·99417 | 4·00 | 3·20 | 0·99085 | 6·50 | 5·21 | 0·98777 | 9·00 | 7·23 |
| 0·99701 | 2·00 | 1·59 | 0·99349 | 4·50 | 3·60 | 0·99021 | 7·00 | 5·61 | 0·98719 | 9·50 | 7·64 |
| 0·98660 | 10·00 | 8·04 | 0·98381 | 12·50 | 10·08 | 0·98114 | 15·00 | 12·13 | 0·97859 | 17·50 | 14·19 |
| 0·98603 | 10·50 | 8·45 | 0·98326 | 13·00 | 10·49 | 0·98063 | 15·50 | 12·54 | 0·97808 | 18·00 | 14·60 |
| 0·98546 | 11·00 | 8·86 | 0·98273 | 13·50 | 10·90 | 0·98011 | 16·00 | 12·95 | 0·97758 | 18·50 | 15·02 |
| 0·98491 | 11·50 | 9·27 | 0·98219 | 14·00 | 11·31 | 0·97960 | 16·50 | 13·37 | 0·97708 | 19·00 | 15·43 |
| 0·98435 | 12·00 | 9·67 | 0·98167 | 14·50 | 11·72 | 0·97909 | 17·00 | 13·78 | 0·97658 | 19·50 | 15·84 |
| 0·97608 | 20·00 | 16·26 | 0·97355 | 22·50 | 18·34 | 0·97097 | 25·00 | 20·43 | 0·96828 | 27·50 | 22·54 |
| 0·97558 | 20·50 | 16·67 | 0·97304 | 23·00 | 18·76 | 0·97044 | 25·50 | 20·85 | 0·96772 | 28·00 | 22·96 |
| 0·97507 | 21·00 | 17·09 | 0·97253 | 23·50 | 19·17 | 0·96991 | 26·00 | 21·27 | 0·96715 | 28·50 | 23·38 |
| 0·97457 | 21·50 | 17·51 | 0·97201 | 24·00 | 19·59 | 0·96937 | 26·50 | 21·69 | 0·96658 | 29·00 | 23·81 |
| 0·97406 | 22·00 | 17·92 | 0·97149 | 24·50 | 20·01 | 0·96883 | 27·00 | 22·11 | 0·96600 | 29·50 | 24·23 |
| 0·96541 | 30·00 | 24·66 | 0·96235 | 32·50 | 26·80 | 0·95910 | 35·00 | 28·96 | 0·95560 | 37·50 | 31·14 |
| 0·96181 | 30·50 | 25·08 | 0·96172 | 33·00 | 27·23 | 0·95842 | 35·50 | 29·39 | 0·95487 | 38·00 | 31·58 |
| 0·96421 | 31·00 | 25·51 | 0·96108 | 33·50 | 27·66 | 0·95773 | 36·00 | 29·83 | 0·95413 | 38·50 | 32·03 |
| 0·96360 | 31·50 | 25·94 | 0·96043 | 34·00 | 28·09 | 0·95703 | 36·50 | 30·26 | 0·95338 | 39·00 | 32·46 |
| 0·96298 | 32·00 | 26·37 | 0·95977 | 34·50 | 28·52 | 0·95632 | 37·00 | 30·70 | 0·95262 | 39·50 | 32·90 |
| 0·95185 | 40·00 | 33·35 | 0·94786 | 42·50 | 35·58 | 0·94364 | 45·00 | 37·84 | 0·93916 | 47·50 | 40·13 |
| 0·95107 | 40·50 | 33·79 | 0·94704 | 43·00 | 36·03 | 0·94276 | 45·50 | 38·30 | 0·93824 | 48·00 | 40·60 |
| 0·95028 | 41·00 | 34·24 | 0·94620 | 43·50 | 36·48 | 0·94188 | 46·00 | 38·75 | 0·93730 | 48·50 | 41·06 |
| 0·94948 | 41·50 | 34·68 | 0·94536 | 44·00 | 36·93 | 0·94098 | 46·50 | 39·21 | 0·93636 | 49·00 | 41·52 |
| 0·94868 | 42·00 | 35·13 | 0·94450 | 44·50 | 37·39 | 0·94008 | 47·00 | 39·67 | 0·93540 | 49·50 | 41·99 |

= Percentage of absolute alcohol by weight contained in the sample. 100 parts of alcohol correspond to 169·2 parts of starch.

If malt extract is used to effect the diastatic conversion of the starch, it will be necessary to conduct a blank experiment with an equal quantity of the extract, yeast and water, and deduct the alcohol formed from this from the total alcohol formed in the determination proper.

The above method for estimating alcohol is commonly applied to beers, wines and spirits. It is used largely for the determination of the "original gravity" of fermented worts, *i.e.*, the specific gravity of the wort before fermentation, for excise purposes. The "original gravity apparatus" consists essentially of a distilling flask connected to a vertically placed spiral condenser, of certain dimensions; by determining the specific gravities of the still residue and the distillate, both diluted to the original volume of the sample, it is possible to calculate the number of "degrees of specific gravity" lost by the wort during fermentation.

In determining the alcohol in beer, 100 c.c. of the sample may be distilled till 80 c.c. of distillate have been collected. Spirits containing about 50 per cent. or more of alcohol should be diluted before distilling; thus, 50 c.c. of the sample may be diluted with 100 c.c. of distilled water, and distilled until the distillate measures 100 c.c.

In order to illustrate the difference in the amounts of alcohol formed from starch in the case when diastase and yeast are allowed to act together, and in the case when the yeast is only allowed to act after the diastase has been destroyed, the above determination of starch as alcohol may be repeated with an equal quantity of

material from the same sample, with the sole difference that the mixture is boiled for 10 minutes in order to destroy the diastase after the diastatic fermentation is complete; the yeast is to be added after cooling to 26° to 27°, and allowed to act at this temperature as described above. All other conditions being equal, the amount of alcohol formed in this case should be less than in the preceding case.

## Malt and Malt Extract.

Under this heading, a method is described by which the relative diastatic activity of diastase or malt extract will be determined in terms of what is known as the "Lintner Value." The value of a malt extract for brewing purposes depends very largely on its diastatic activity, *i.e.*, on the ability of the diastase which it contains, to effect a rapid conversion of the starch into maltose and dextrin; for the purpose of the last two analytical processes described for the determination of starch, it is also desirable that the diastase or malt extract used should be fairly active. If commercial malt extracts are employed, it is desirable that their diastatic activity should be determined before use, as many preparations on the market have little or no power to effect the hydrolysis of starch.

Before the determination is described, a few words may be said regarding the preparation and composition of malt. Malt is prepared by steeping barley in water and then allowing it to germinate at a suitable temperature; during this process, diastase, as well as other enzymes, are formed in order that the starch may be converted into soluble products which can be assimilated by the growing embryo. Before germination has proceeded to any extent, the vital processes are stopped by drying and curing the grain in a kiln; the action of the diastase on the starch and other carbohydrates is thereby stopped for the time being, to be continued when the malt is subsequently made into a mash with water.

During the drying process, various substances are formed which impart colour and flavour to the malt and to the products prepared from it.

Malt varies in colour from light yellow to dark brown, according to the origin of the barley and the degree of the curing, or drying. It should be crisp and white inside; its diastatic activity depends very largely on the freshness and quality of the grain from which it is prepared, as well as on the degree of curing.

The following typical analysis, from Blount and Bloxam's "Chemistry for Engineers and Manufacturers,"[1] will give an idea of the approximate composition of barley and malt; the most noticeable differences, on the analytical figures, between barley and malt are the lower proportion of water and the higher proportion of soluble carbohydrates contained in the latter. Further, malt usually contains slightly less fatty matter, and more soluble nitrogen compounds than barley.

| —— | Barley. | Malt. |
|---|---|---|
| | Per cent. | Per cent. |
| Water . . | 14·1 | 5·8 |
| Proteins . . | 10·6 | 13·1 |
| Fat . . . | 2·1 | 1·7 |
| Carbohydrates . | 63·7 (mainly starch). | 65·4 (about $\frac{1}{3}$ being fermentable sugar) |
| Fibre . . | 7·1 | 11·6 |
| Ash . . | 2·6 | 2·6 |

*Determination of the Diastatic Activity* (*Lintner Value*) *of Malt.*[2]—This determination is based on Kjeldahl's observation that in malt diastase conversions, where the

[1] See also the figures given under the headings, "The Examination and Analysis of Barley" (p. 270), and "The Examination and Analysis of Malt" (p. 273).
[2] See also the Saccharification Test (p. 274).

amount of maltose formed does not exceed 45 per cent. of the starch originally present, the amount of maltose produced in a given time may be taken as a measure of the activity of the diastase solution used. The actual method described is due to Lintner. In the first place, the preparation of soluble starch and the malt extract will be described.

*Preparation of Soluble Starch.*—This may either be obtained ready-made or prepared as follows: 100 grams of purified potato starch are digested with 500 c.c. of dilute hydrochloric acid of specific gravity 1·037, at the ordinary temperature, for 7 days, the mixture being stirred daily. The mass is then washed repeatedly by decantation, first with tap water and then with distilled water, till all the acid has been removed. When the moist starch gives no acid reaction when spread on blue litmus paper, a few drops of dilute ammonia are added, and the starch again washed by decantation until all the ammonia has been removed. It is then collected on a Buchner funnel, sucked as dry as possible, spread on a porous plate and dried at a gentle heat (about 30°). When required for use, the pulverised starch is dissolved in boiling water to make a 2 per cent. solution which, on cooling, should be perfectly mobile, and not gelatinous, as would be the case with a solution of untreated starch. Its action on Fehling's solution, on boiling, should be negligible.

*Preparation of Malt Extract.*—25 grams of the finely ground malt are extracted with 500 c.c. of distilled water for 3 hours at 21°, agitating the mixture from time to time. The whole is then filtered, the first 100 c.c. of the filtrate being rejected. The extract obtained should be perfectly clear and bright.

The actual determination of diastatic activity is carried out as follows: Portions of 10 c.c. of a 2 per cent.

solution of soluble starch are measured out in eight carefully cleaned test tubes, which are placed in a suitable stand and immersed in a water bath kept at 21°. When the starch solution has reached the temperature of the bath, 0·1 c.c. of the malt extract to be tested is measured into the first tube, 0·2 c.c. into the second, 0·3 into the third, and so on, to the eighth tube, into which 0·8 c.c. will be introduced. In examining pale malts, *i.e.*, malts which usually have a relatively high diastatic power owing to the lightness of the curing, it is recommended to dilute the extract obtained as directed above with an equal volume of water, and to add it to the starch solution in the tubes, in amounts of 0·2 c.c., 0·3 c.c., 0·4 c.c., etc. ; in this way, greater accuracy will be attained. The tubes are allowed to remain in the water bath at 21°, for exactly 1 hour from the time the extract has been added. 5 c.c. of mixed Fehling's solution (see p. 139) are then added to each tube, and after shaking the tubes are heated in boiling water for 10 minutes and allowed to stand until the cuprous oxide has settled. Usually the liquid in one of the tubes is faintly blue, showing that the maltose present was insufficient in amount to effect the complete reduction of the cupric salt present in the 5 c.c. of Fehling's solution, while the liquid in the next tube of the series is yellow, owing to over reduction. In this way the amount of malt extract which is just sufficient to produce, in the given time, the quantity of maltose to reduce 5 c.c. of Fehling's solution may be estimated. Thus, if tube No. 2 is as much under reduced as tube No. 3 is over reduced, then the amount of malt extract sufficient to cause complete reduction may be taken at 0·25 c.c. (*i.e.*, if tube No. 2 contained 0·2 c.c., and tube No. 3 contained 0·3 c.c. of the extract). If the liquid in one of the tubes is neither

blue nor yellow, then the maltose formed therein will have been just sufficient to cause complete reduction.

Complete reduction by 0·1 c.c. of malt extract corresponds to a Lintner value of 100. If X is the quantity of malt extract required for complete reduction, in cubic centimetres, then the diastatic activity of the malt,

$$A = \frac{0 \cdot 1 \times 100}{X}.$$

From the figure thus found, it is usual to deduct 1·5, to allow for the reducing sugars present in the malt extract. If the extract has been diluted with an equal quantity of water, then half the volume actually added must be used for the purposes of the calculation.

Diastatic activities of over 80 are considered high, under 50 low.

The examination of malt is further described below. (See p. 273.)

## FLOUR.

### INTRODUCTORY.

The most important of the starch-containing food materials are derived from the grain of the cereals, such as wheat, rye, maize, barley, etc., after removal of the chaff (paleæ and glumes) by threshing. The coarsely ground grain is known as meal, the finely ground grain as flour. Special attention is paid to the examination of wheaten flour, as this is the most important of the flours consumed in this country, as well as being the dearest, and therefore the most likely to be adulterated with other flours.

The following table contains results published by the United States Department of Agriculture, showing the average composition (percentage) of the more important cereals; a typical analysis of potato is appended.

The products obtained from the grain of wheat on milling may be divided into the flour proper, by which is understood the contents of the parenchymatous cells

| Description of Grain. | Moisture. | Nitrogen × 6·25. | Crude Fibre. | Ash. | Carbohydrates other than Crude Fibre. | Ether Extract (chiefly fat). | Weight of 100 Kernels in Grams. |
|---|---|---|---|---|---|---|---|
| Typical unhulled barley | 10·85 | 11·0 | 3·85 | 2·5 | 69·55 | 2.25 | — |
| Typical American maize | 10·75 | 10·0 | 1·75 | 1·5 | 71·75 | 4·25 | 38·0 |
| Typical rye | 10·5 | 12·25 | 2·1 | 1·9 | 71·75 | 1·5 | 2·5 |
| Typical unhulled oats | 10·0 | 12·0 | 12·0 | 3·4 | 58·0 | 4·5 | 3·0 |
| Typical rice, unhulled | 10·5 | 7·5 | 9·0 | 4·0 | 67·4 | 1·6 | 3·0 |
| Typical rice, polished | 12·4 | 7·5 | 0·4 | 0·5 | 78·8 | 0·4 | 2·2 |
| Typical wheat | 3·85 | 12·25 | 2·4 | 1·75 | 71·25 | 1·75 | 3·85 |
| Potato | 74·7 | 2·0 | 1·4 | 1·0 | 20·7 | 0·2 | — |

of the endosperm, and the offal, which includes the bran, or husk, the germ, *i.e.*, the embryo plant, and fluffy or fibrous matter derived from the cell walls of the parenchymatous endosperm ; "sharps," or "middlings," consist of finely divided bran with particles of germ. The commercial valuation of flours varies according to the amount of offal which they contain, the highest grade being the so-called "patent flour" which, owing to its freedom from offal, is the whitest in colour and most homogeneous product ; it is appreciated by bakers on account of the amount of water which it will absorb and the appearance of the loaf which it produces, though as regards nutritive value it is not necessarily superior to the lower grades. "Wholemeal," or "Graham," flour is the product of grinding of the entire wheat grain, including the husk and germ ; it should have the same composition as the wheat grain itself ; containing the whole of the offal, it is considerably darker in colour than patent flour, and not being subjected to any sifting process, it contains branny particles which are distinctly visible. The so-called "entire wheat flour," or fine meal, is the product obtained by removing a portion of the bran and finely grinding the rest of the grain ; the texture is somewhat coarser than

that of ordinary or patent flour, the colour and general appearance varying somewhat, according to the amount of offal removed and the nature of the wheat from which it is milled. "Entire" flour usually contains a portion of the germ. "Standard," or 80 per cent. flour, may be classed as an "entire" flour, representing 80 per cent. of the wheat grain, and containing the whole of the germ.

"Households grade" is the commercially lower grade of flour which is produced besides the patent grade in the modern process of roller milling; it is darkish in colour and contains a small amount of fine branny particles; from the baker's point of view, it is inferior to patent flour in bread making. "Baker's grade" and "clear grade" are terms applied to similar grades in America. "Straight run," or "straight grade," may be regarded as a mixture of the patent and household grades.

Special flours may be prepared from any of the above grades, usually with a view to improving the nutritive value. They may contain finely powdered bran, lentil flour or banana meal. Germ flours contain added germ (usually cooked).

The above is an abridged version of Dr. Hamill's classification of the various flours on the market, included in his report to the Local Government Board on the nutritive value of bread made from different varieties of wheat flour. As is pointed out by Dr. Hamill, it is very difficult to set up analytical standards for defining any particular grade of flour, owing to the difference in composition of wheats from different sources. Comparisons of the composition of different grades of flour can only be of value when these are milled from the same wheat.

The following table, compiled by the United States Department of Agriculture, shows the variations in the composition of wheats from different sources:—

| | Per cent. |
|---|---|
| Water | 7 to 14 |
| Proteins | 8 ,, 17 |
| Dry gluten | 2 ,, 14 |
| Carbohydrates | 65 ,, 76 |
| Ether extract (chiefly fat) | 0·28 ,, 2·5 |
| Ash | 1·4 ,, 2·3 |

A number of analyses of various flours and other milling products obtained from different wheat mixtures are given in Dr. Hamill's report. From these and from the figures given in the next table, it will be seen that the presence of bran in the flour tends to raise the content of mineral matter and crude fibre. The presence of germ tends to raise the content of fat and protein, but usually these increases are comparatively insignificant. "Germ flours" may, however, contain as much as 4 to 5 per cent. of additional protein due to added germ.

The following table from Wynter Blyth's "Foods, their Composition and Analysis," shows the compositions of various flours of different grades, the original wheat from which these are milled, and of the bran. The superiority of grade and freedom from bran decrease from Nos. 0 to 9:—

| Description of Flour of Varying Grades as obtained from Steel Roller Mills and Bran. | Per Cent. Yield on Original Wheat. | Water. | Insoluble Nitrogenous Matter. | Soluble Nitrogenous Matter.[1] | Fat. | Carbohydrates other than Crude Fibre. | Crude Fibre. | Ash. |
|---|---|---|---|---|---|---|---|---|
| Original wheat | — | 13·37 | 10·69 | 2·93 | 1·98 | 80·41 | 1·90 | 2·09 |
| Flour No. 0 | 6·0 | 12·56 | 8·38 | 3·06 | 0·83 | 87·26 | trace. | 0·47 |
| " " 2 | 6·0 | 12·48 | 8·87 | 2·95 | 0·97 | 86·69 | " | 0·52 |
| " " 6 | 4·0 | 12·39 | 9·38 | 3·00 | 1·17 | 85·87 | 0·02 | 0·56 |
| " " 8 | 5 to 6 | 11·72 to 12·41 | 10·06 to 14·34 | 2·72 to 3·22 | 1·30 to 3·51 | 75·90 to 84·55 | 0·06 to 1·03 | 0·81 to 2·23 |
| " " 9 | 3·0 | 10·64 | 15·02 | 2·55 | 4·02 | 74·20 | 1·55 | 2·66 |
| Fine bran | 16·0 | 11·35 | 13·50 | 3·06 | 4·54 | 63·64 | 8·71 | 6·55 |
| Coarse bran | 2·0 | 12·37 | 13·44 | 3·17 | 3·46 | 62·13 | 9·79 | 8·01 |

[1] Soluble nitrogen, estimated by Weinwurm, according to the method described below.

The crude fibre is the cellulose vegetable tissue which is insoluble in dilute boiling acid and alkali; it cannot be looked on as a definite constituent, the amount found varying somewhat according to the method of estimation. On examination of the ash, or mineral matter, the principal bases which will be found are potash, lime and magnesia, and the principal acid, phosphoric acid. The nitrogenous constituents of wheat flour may be divided

into the gluten and the soluble nitrogen compounds; they are of importance, not only on account of their nutritive value, but also on account of the texture which they impart to the bread. Gluten consists mainly of two proteins, gliadin and glutenin. The former is a soft, sticky substance which can be pulled out into threads; it may be separated from the other constituents of flour by extraction with 70 per cent. alcohol, in which it is soluble, and by precipitation from this solution by the addition of an aqueous solution of sodium chloride. Though soluble in pure water, gliadin is not dissolved when flour is treated with water, owing to the presence of mineral salts. Glutenin is distinguished by its solubility in very dilute alkali solution; it is of a firmer consistency than gliadin; the latter imparts tenacity to the gluten, and on this account, bakers usually prefer a flour containing a high percentage of gliadin. The proteins other than gluten include a globulin, an albumin and a proteose; these are probably of greater nutritive value than the gluten.

## The Examination and Analysis of Flour.

As has been previously pointed out, the commercial value of wheat flour depends on its colour, texture, and the amount and nature of the gluten present. The highest grade flours should be practically white, showing only the faintest tinge of yellow; they should possess a sweet smell and be free from branny particles and acidity. By the tests and analytical methods now to be described, the quality of a flour may be gauged to a certain extent; a great deal, however, depends on the appearance of the flour and the loaf which it will make. The detection of added foreign matter and foreign flours will also be dealt with.

*Gluten Test.*—In this test, the gluten is separated from the other constituents of the flour by mechanical means, examined and estimated. About 30 grams of flour are made into a stiff dough with about 12 to 15 c.c. of water, and allowed to stand for an hour. The mass is then

carefully kneaded in a stream of running water, over muslin until all the starch has been removed. The fresh gluten thus obtained should only have a faint yellow tinge and should be of such a consistency that it can be pulled out into threads ; the gluten from English wheat is usually very soft and sticky, having less elasticity than gluten from other wheats. A dark and viscous gluten indicates the presence of rye flour ; most of the other common flours also give more or less coloured glutens, thus, that from barley is non-viscous and dirty reddish brown, from oats, dark yellow, from maize yellowish and non-elastic, from leguminous flours such as those of the bean or pea, greyish red to green. A grey or reddish gluten may also be obtained from inferior wheat flour. After washing, the gluten is left under water for an hour, after which the excess of water is removed as completely as possible by pressing with the hands, and the moist gluten weighed. It is then dried at 100° till constant in weight, which may take 24 hours or more. A good wheat flour will contain from 20 to 40 per cent. of moist gluten and about 10 to 18 per cent. of gluten dried at 100°. When heated to 150°, good gluten swells and assumes the appearance of bread.

The above test, although useful for valuating flour, cannot, of course, be looked on as an accurate analytical process ; the gluten obtained will contain small percentages of non-gluten proteins, mineral matter, fat, starch, fibre, etc.

*Total Proteins.*—The total nitrogen is determined in about 2 to 3 grams of the original flour by the Kjeldahl method, as described in Chapter I., p. 22. The nitrogen present as nitrates, which exist in small quantity in wheat, will, of course, not be converted into ammonia and estimated by this method (see p. 26). The average

nitrogen content of wheat proteins being 17·6 per cent., the nitrogen found should be multiplied by 5·68, in order to give the total proteins. For many other cereal proteins, the factor 6·25 gives a more accurate result. Reference to the last table will show that there is a tendency for the protein content to increase in passing from the high-grade flours, through the lower-grade flours, to bran. In this connection, however, it must be remembered that the protein content of wheat from different sources varies within fairly wide limits (see the previous tables). As was pointed out above, the inclusion of the germ in the flour will not materially raise the protein content, though if much extra germ be added, as in the case of the so-called germ flours, the protein content may be raised by as much as 4 to 5 per cent. above the normal.

According to the United States standard of purity, wheat flour must contain not less than 1·25 per cent. of nitrogen.

*Gliadin.*—This may be estimated by extracting the flour for 2 hours with 70 per cent. alcohol, filtering, and determining the nitrogen in an aliquot portion of the filtrate. For conversion of the nitrogen found into gliadin the factor 5·68 should be used.

In a good flour the gliadin should constitute about 60 per cent. or more of the total gluten.

*Soluble Nitrogenous Matter.*—This is estimated by Weinwurm as follows: 10 grams of the material are treated with 200 c.c. of hot water and 0·5 c.c. of acetic acid, and the whole is warmed on a water bath for 20 minutes. The solution is cooled, made up to 500 c.c., and filtered; the soluble nitrogen is then estimated in 50 c.c. of the filtrate, which should be evaporated nearly

to dryness before adding the sulphuric acid for the Kjeldahl estimation. Our knowledge regarding the relative digestibility of the various proteins of the cereals is somewhat limited, though it may be presumed that the soluble nitrogenous matter as estimated by the above method has greater nutritive value than the proteins of the gluten. Several other methods have been devised for estimating the "digestible nitrogenous matter."

*Water.*—1 to 3 grams of the flour are weighed out between watch glasses, and dried in a steam oven till no further loss in weight takes place.

In the United States and Canada, the maximum limit for water in flour is fixed at 13 per cent. An unduly large proportion of water impairs the keeping qualities of the flour, besides, of course, lessening its nutritive value.

*Ash.*—About 5 grams of the flour are burnt in a crucible, in a muffle furnace, and the residual ash weighed. An alternative method which is sometimes used is to mix the flour with powdered ammonium nitrate, heating the mixture carefully and withdrawing the flame directly fusion commences. In this way, the flour may be burnt up quickly, without the use of the muffle furnace. A corresponding quantity of ammonium nitrate should be heated separately, and the residue which it leaves, if any, determined and deducted from the ash found in the actual estimation.

The amount of ash or mineral matter present in the patent and other higher grades of flour is usually under 0·5 per cent.; households and "standard," or 80 per cent. flour, generally contain between 0·5 and 0·9 per cent. of mineral matter, while wholemeal may contain between 1·5 and 2 per cent., or even more. From a study of the table on p. 255, it will be obvious that the greater the proportion of bran or offal left in the flour, the more

mineral matter will the latter contain. According to the United States standard of purity, wheat flour should not yield more than 1·0 per cent. of ash. If the amount of ash found seems abnormally high in relation to the quality of the flour, it is possible that mineral matter has been added with a view to improving its appearance. Acid potassium, magnesium or calcium phosphates may sometimes be added as "improvers" in the proportion of about 0·5 per cent. of the flour. If such additions are suspected, the ash should be preserved for further examination. Alum and copper sulphate may also be used as improvers, but the quantities added will be too small to be detected by any increase in the proportion of the ash. Self-raising flours usually contain added sodium bicarbonate and acid calcium phosphate, these constituents sometimes being added in the proportion of about 3 per cent. of the flour. The detection of added mineral matter will be dealt with later.

*Starch.*—This is best estimated by O'Sullivan's method, described on pp. 236 *et seq.*

*Acidity.*—20 grams of the flour are shaken with 200 c.c. of water at intervals, for 2 hours, the mixture is filtered, and 50 c.c. of the filtrate titrated with decinormal sodium hydroxide solution, using phenol phthalein as indicator.

According to Wynter Blyth, normal wheat should show an acidity corresponding to not more than 0·16 to 0·25 per cent. of lactic acid. The test is useful for detecting the presence of unsound wheat in flour.

*Fat (Ether Extract).*—This is determined by extracting about 3 grams of well-dried flour with ether in a Soxhlet apparatus. (See p. 66.) The extracted material should be preserved for the estimation of crude fibre. When the extraction is complete, the ethereal solution is evaporated in a tared flask, the residue dried at 105°, and weighed.

Although, generally speaking, it may be said that the greater the proportion of bran in the flour the higher the fat percentage (see the table on p. 255), the latter can hardly be taken as an index of the quality of the flour, chiefly owing to the variations in the fat content of flours from different sources.

*Crude Fibre.*—The following method is recommended by the American Association of Official Agricultural Chemists for the estimation of crude fibre in grain, flour, and bye-product cattle foods, such as oil cake, etc.: 2 grams of the material are extracted with ether, or the extracted material from the fat determination may be used. The fat free material is placed in a 500 c.c. flask, and 200 c.c. of boiling 1·25 per cent. sulphuric acid are added; the flask is connected with a reflux condenser by means of a rubber stopper; boiling is commenced at once and continued for 30 minutes. A current of air passing through the liquid may serve to reduce frothing. The mixture is filtered, and the residue washed with boiling water until the washings are no longer acid; it is then rinsed back into the same flask with 200 c.c. of a boiling 1·25 per cent. solution of sodium hydroxide, free or nearly so, from carbonate; boiling is commenced at once, and continued for 30 minutes, in the same manner as directed above for the treatment with acid. The insoluble residue is filtered off on a Gooch crucible and washed with boiling water until the washings are neutral, dried at 110° and weighed; it is then incinerated completely; the loss in weight thus occasioned represents crude fibre.

The filter used for the first filtration may be of linen, glass wool, asbestos or any convenient form giving clear and reasonably rapid filtration. The strength of the acid and alkali solutions employed should be verified by titration, and not merely by the specific gravity.

According to the United States standard of purity,

wheat flour should not contain more than 0·5 per cent. of crude fibre. As will be seen from the table on p. 255, the crude fibre in the highest grades of wheat flour only amounts to traces, and increases with the proportion of bran present. Provided that a perfectly uniform method of estimation is adopted, the percentage of crude fibre is, perhaps, the most reliable index of the amount of branny matter in the flour.

### The Detection and Estimation of Foreign Matter and Adulterants in Wheat Flour.

Under this heading the detection of added mineral matter, foreign flours or starches, and flour damaged by fungi, such as ergot, are considered. Added mineral matter cannot, as a rule, be detected with any certainty by an increase in the ash content of the flour, owing to the variations in ash content of flours of differing fineness and origin; for this purpose, the special methods described below must be adopted. Addition of foreign flours, etc., may sometimes be detected by the use of the microscope, though for this task considerable experience is often necessary. In some cases, however, chemical methods are available.

*Alum.*—Alum is sometimes added to bad or slightly damaged flour by the miller or the baker in order to improve its appearance; although it is only added in very small quantities, which can hardly be injurious to health, its use is prohibited by law in England. Two methods are available for the detection of alum in flour, *i.e.*, the logwood method and the chloroform method; the latter method also allows of the detection of mineral additions other than alum.

*Logwood Method.*—Tincture of logwood, which should always be freshly made, is prepared as follows: ½ gram of fine logwood chips, preferably cut fresh from the log, is macerated for 10 hours in 15 c.c. of alcohol; 10 c.c. of the solution are poured off and mixed with 150 c.c. of water and 10 c.c. of a saturated solution of ammonium

carbonate. The test should be carried out immediately after the addition of the ammonium carbonate; 50 grams of the flour are made into a thin paste with water, a few drops of the logwood solution are added, and the mixture allowed to stand for several hours. If alum is present a lavender blue lake will be produced. The colour should persist when the sample is placed in an oven at 100° for 2 hours. If only 1 part of alum in 1,000 be present, the flour becomes pink instead of lavender. In the case of a negative result being obtained by this test, the absence of alum may be inferred. If a positive result is obtained, it is best to confirm it by the chloroform method in order to make sure that the coloration is not due to adventitious clayey matter from the mill-stones; in the modern process of milling, however, in which steel rollers are used, the latter source of contamination is avoided. Moreover, the logwood test is only obtained in the presence of aluminium compounds soluble in water.

*Chloroform Method.*—This method also allows of the detection of mineral matter other than alum; as mentioned above, alum and copper sulphate are only added in very small quantities, their function being to increase the whiteness of the flour; their use is forbidden by law, and it is but rarely that they will be found in commercial samples of flour. Substances such as acid potassium, magnesium or calcium phosphates, notably the latter, are used in larger quantities, their function likewise being to make lower grades of flour appear equal to the highest grades; they are said to "make the flour bake whiter, while the bread is improved in boldness, texture, crust, etc." Dr. Hamill, in his report to the Local Government Board on the bleaching of flour and the addition of so-called "improvers" to flour, states that he has seen acid calcium phosphate added to, and intimately mixed with, flour in the proportion of about 0·45 per cent. of the finished flour. Curtel

(*Annales des Falsifications*, 1910, p. 302) describes a preparation sold under the name "Blanc Flour," consisting essentially of acid calcium phosphate, which the makers recommend should be added in the proportion of 1 per cent. of the flour. Considerable quantities of calcium sulphate may be introduced if inferior grades of calcium phosphate are used, especially in the case of self-raising flours, which are now usually prepared by adding calcium acid phosphate and sodium bicarbonate to the flour. As mentioned above, the amount of mineral matter added in such cases is usually large enough to be detected by an examination of the ash of the flour. In a report to the Local Government Board it is recommended that bakers and millers should insist on a calcium phosphate containing under 10 per cent. of calcium sulphate. If a conspicuous excess of the latter be found, prosecution under the Sale of Foods and Drugs Act of 1875 might be considered.

The detection of added mineral matter by the chloroform method may be carried out as follows: 200 grams of flour are shaken in a separating funnel with sufficient chloroform to give a perfectly liquid mixture, and allowed to stand overnight. The chloroform is of sufficient density to float the organic constituents of the flour, while the mineral matter will sink to the bottom, without being dissolved. The solid matter which has collected at the bottom is carefully removed through the stopcock, shaken a second time with a little more chloroform, and when it has subsided again, transferred to a watch glass so that the chloroform may evaporate. The residue is treated with a small quantity of water, the solution is separated from the insoluble portion and allowed to evaporate, when the alum will separate, if present, in the form of octahedral crystals, which may be identified by examination under a low-power microscope. The crystals may be dissolved in water, and identified as alum by the usual tests. The residue insoluble in water may

be examined under the microscope, and subjected to a qualitative analysis for metals and acid radicles; small amounts of copper salts, either in the soluble or insoluble portion, may be detected by their delicate reaction with potassium ferrocyanide.

For the detection of calcium phosphate in flour, Curtel (*loc. cit.*) recommends the following method, which, in principle, is practically identical with the foregoing: 5 grams of flour are shaken with 40 to 50 c.c. of carbon tetrachloride, the mixture is centrifuged, and the flour and the carbon tetrachloride are separated from the sediment; the latter is dissolved in a little nitric acid, and tested with a small quantity of ammonium molybdate solution; if the flour contained added calcium phosphate, a copious precipitate will be obtained; the small amount of sediment obtained from unadulterated flours, representing natural impurities, will produce no precipitate. The use of the centrifuge, both in this and the forgeoing method, greatly facilitates the separation of the mineral sediment from the flour. The advantage of the two methods just described lies in the fact that practically only the mechanically admixed matter is separated; moreover, by the use of such liquids as chloroform or carbon tetrachloride, interaction between the added mineral matter and the natural constituents of the wheat is avoided, such as, for example, would occur between alum and the wheat phosphates in presence of water.

*Detection of Flour Damaged by Moulds.*—After bad seasons, flour is liable to contain matter which has been damaged by moulds, especially ergot. For the detection of starch which has been affected by moulds, a minute quantity of the flour may be mounted in a drop of glycerol, and examined under a low-power microscope;

a drop of aniline violet solution is then allowed to diffuse into the mounting medium, under the cover glass; granules which have been damaged by mould of any kind will take up the colour intensely.

*Chemical Method for Detecting Ergot.*—The following method is given by Leffmann and Beam: 10 grams of flour are macerated for about 30 minutes with a mixture of 20 c.c. of ether and 10 drops of dilute sulphuric acid (1 to 5 parts water); the mixture is filtered and the residue is washed with ether until the filtrate measures 15 c.c. This filtrate is shaken up with 5 drops of a saturated solution of sodium bicarbonate. The green chlorophyll remains in the ether; the bicarbonate solution will remain clear if the flour be derived from sound grain, but becomes deep violet if ergot be present.

The sale of ergotised flour as good flour would constitute an offence under the Sale of Foods and Drugs Act.

*The Detection of Foreign Flours in Wheat Flour.*—According to Wynter Blyth the following have been fraudulently added to flour: rye, rice and barley meals, flours from various leguminosae, such as the bean or pea, linseed meal, buckwheat, potato and some other starches. Such additions are stated to be rare in this country, the foreign flours most likely to be met with being those of rice and the potato; adulterations of this nature are, naturally, most frequently to be met with in practice in times of scarcity of wheat.

*General Tests.*—Vogel extracts the suspected flour with 70 per cent. alcohol, to which 5 per cent. of hydrochloric acid has been added; if the flour is derived from pure wheat or rye, the alcohol remains colourless, but takes up a yellow colour if either barley or oats be present, orange yellow in presence of pea-flour, and purple red or blood red in presence of mildewed or ergotised wheat, respectively.

The conclusions which may be drawn from the appearance of the gluten, are given under the gluten test. (See p. 256.) Special methods for the detection of foreign flours will now be described.

*Potato Starch.*—Donné's test for the detection of potato starch in wheat flour is carried out as follows: the flour is examined in a thin layer, mounted in water, in the usual way, under the microscope; then, while the starch is still under observation, a weak solution of potassium hydroxide is allowed to diffuse under the cover glass. Under the influence of the alkali, potato starch granules will begin to swell till they reach 4 to 5 times their original volume, while wheat starch is scarcely affected. In order to render this test sharper, it may be combined with Lecanu's subsidence process, when it will be possible to detect as little as 1 part of potato starch in a thousand of wheat flour.

The process just alluded to depends on the fact that potato starch has a higher specific gravity than wheat starch, and will consequently sink in water sooner than the latter. 100 grams of the flour are made into a dough with water, and the gluten is separated by kneading in water; the wash water is collected, stirred and passed through a sieve to separate the coarser suspended matter, and then allowed to stand in a conical flask until a deposit has formed. The supernatant liquor is decanted while still turbid, and the deposit stirred up with more water and allowed to stand for a short time. After decanting the turbid supernatant liquor, the process is repeated once more, when the lowest portion of the final deposit will consist entirely of potato starch, if this be present. The influence of dilute potassium hydroxide solution on the starch grains may then be studied by means of the microscope, as directed

above. Comparison should be made with a genuine sample of unadulterated wheat.

*Leguminous Starches.*—Leguminous starches may be detected with comparative ease in wheat flour by microscopic examination. If a thin layer of the flour be mounted in a mixture of water and glycerol, in the proportion of 2 parts of the former to 1 of the latter, and examined under the microscope between crossed Nicol prisms, a selenite plate being interposed between the object and the lower Nicol prism, the leguminous starches will show no play of colours, and will easily be detected among the iridescent starch granules of wheat. Further, if the flour is treated under the microscope with a 10 to 12 per cent. solution of potassium hydroxide, it will be possible to dissolve the starch of the leguminosae, leaving a characteristic reticular tissue, made up, for the most part, of irregular hexagons.

*Separation of Legumin.*—Leguminous starches may be detected by the separation of legumin, a constituent peculiar to this group. Lecanu's process is as follows: The gluten is separated in the usual manner, as described above under the gluten test, the wash water, which contains the starch, soluble matter and legumin, being collected, passed through a sieve to separate the coarser suspended matter, diluted, if necessary, and allowed to settle. The supernatant liquid is divided into 2 parts; one of these is allowed to putrefy or ferment spontaneously; with pure wheat flour, lactic acid fermentation is the most common; with flours containing legumin, putrefactive fermentation will set in at once. In lactic acid fermentations, the principal change which occurs is the transformation of sugar into lactic acid, a change which may be followed by noting the increasing acidity of the liquid; in putrefactive fermentations, the

proteins are decomposed. (See the account of the decomposition of milk by micro-organisms in Chapter VI.)

The second portion of the aqueous extract from the flour is filtered clear, and concentrated by evaporation until a yellowish scum forms on the surface; it is then allowed to cool, and filtered in order to remove the albumen, which, at this stage, will have separated from the flour whether it contains leguminous products or not. The legumin, if present, is precipitated from the filtrate by the addition of a drop of acetic acid, filtered off and dried in the steam oven. When dry, legumin is of a horny consistence, insoluble in alcohol, not coloured by iodine and easily soluble in caustic alkali or ammonia solutions, from which it may be precipitated by the addition of acid. According to Lemenant des Chenais, 0·9 parts of legumin in 100 parts of flour, represents an adulteration corresponding to 5 per cent. of added leguminous flour. Too much reliance should, however, not be placed on a quantitative estimation of this kind.

*Rice Flour.*—Rice flour may be detected in wheat flour by a microscopic examination of the starch granules. Wheat starch, in common with the starches of rye and barley, shows no hilum or concentric rings in the majority of granules, which are nearly circular, and flattened in shape. The granules of rice starch, on the other hand, are polygonal in shape, as viewed under the microscope, show faint rings, and under high magnification, a starred hilum. Gastine advises staining with aniline blue or green (as previously described), which will show up the hilum of the minute starch granules as a reddish point.

In all these microscopic examinations, comparison should always be made with samples which are known to be genuine, as well as with samples which have been purposely adulterated.

## The Examination and Analysis of Barley.

The use of barley for the preparation of malt in the brewing industry has been referred to above. (See p. 248.) The object of the tests described under this heading is to determine the suitability of barley for this purpose.

Barley may vary in colour from whitish yellow to brown, the best usually being that of a bright yellow colour. If too light, the grain may have been bleached by chemical means (sulphurous acid) while if too dark, or coloured brown at the tips, it has probably been unduly exposed to rain. It should possess a sweet smell like that of straw; if musty or mouldy in smell, it has probably been badly harvested or stored. The various outward characteristics by which the expert judges the quality of barley will not be detailed here, and the mechanical tests will only be briefly referred to. The student desiring further information on these points, is referred to the works on the subject of brewing, mentioned at the end of the present chapter.

*Sampling.*—Several portions are taken from different places and depths in the sack or heap, and well mixed; 500 grams are then taken as a sample for analysis, which is preserved in an air-tight vessel.

*Mechanical Tests.*—The more important mechanical tests are as follows: (*a*) Determination of glumes or chaff, which should not amount to more than about 7 to 10 per cent. of the grain (Weber). (*b*) The form and size of the corns may be examined by specially constructed sifting machines; (*c*) the "Sinker" Test; when several hundred corns are thrown into water, only about 2 to 3 per cent. should float; (*d*) the relative transparency of the grain may be observed by means of apparatus specially designed for the purpose; (*e*) the weight of 1000 corns (air dried); (*f*) the weight per hectolitre; (*g*) germination tests. Special apparatus has been designed for carrying out the three last-mentioned tests.

CHEMICAL EXAMINATION.

*Water.*—A weighing bottle, furnished with a glass stopper and measuring about 5 to 6 cm. in height and 3·5 cm. in diameter, is carefully dried (in the air-oven) and weighed after cooling. 5 grains are then ground up in a small hand mill through which a little barley has been passed beforehand, and the meal is immediately weighed out in the closed bottle. After removing the stopper the bottle is placed in an air-oven at about 50° to 60°, the temperature being kept constant for an hour and a half, after which it is raised to 105° and kept at this point for 3 hours. The bottle is then stoppered, cooled and weighed, the loss in weight being calculated to percentage of water, as usual. A low temperature is employed at the outset, in order to prevent the formation of soluble starch and further decomposition of the latter, in the presence of an excess of water.

The water percentage in barley, which may vary from 12 to 18, should be an important factor in its commercial valuation ; a good barley should contain from 13 to 15 per cent. of water.

*Fat.*—The dried residue from the water determination is extracted with ether in the Soxhlet apparatus. (See p. 66.)

Barley may contain from about 1·6 to 2·6 per cent. of fatty matter. Occasionally, however, the barley may have been treated with oil in order to give it a shiny appearance, in which case the fat content as determined by the above method will be materially increased.

*Nitrogen* (*Proteins*).—This is determined on 2 to 3 grams of barley, by the Kjeldahl process. (See p. 22.) The factor for converting nitrogen into proteins is 6·25.

According to Weber, the protein content of barley

may vary from 6 to 18 per cent., but generally speaking, a good barley for brewing purposes should contain not less than 8, and not more than 11 per cent. of proteins. A low protein content affects the yeast unfavourably in the fermentation process, while with a high protein content, the amount of extract obtained from the malt is decreased.

*Starch.*—This constituent may be determined on the finely ground barley by the methods described on pp. 236, 244.

The percentage of starch in barley usually lies between 70 and 80, and furnishes a measure of the proportion of extract obtainable from the malt for brewing purposes. Unfortunately, however, the methods available for the estimation of starch in presence of plant tissues are not as accurate as could be desired.

*Ash.*—This may be determined on the finely ground barley, as described for flour on p. 259.

The content of ash in barley usually lies between 2·5 and 3·5 per cent.

*Test for Bleaching by Sulphur Dioxide.*—Mixed or badly coloured barleys may be made to assume a uniform light yellow colour by treatment with sulphurous acid.

Evidence of such treatment may be obtained as follows: (Weber) 100 grams of the barley are mixed with 100 c.c. of water, stirred at intervals for ½ an hour, and filtered. 100 c.c. of water and a few pieces of pure zinc are placed in a beaker, and sufficient concentrated hydrochloric acid is added to cause a moderately rapid evolution of hydrogen. The beaker is covered with a piece of filter paper, the middle of which has been moistened with a few drops of lead acetate solution. If, after some time, no brown or black stain appears on the paper, the zinc and acid are sufficiently pure, and the test may be proceeded with. The water is poured off

from the zinc, and the filtrate from the barley added in its place, together with a little concentrated hydrochloric acid. Sulphurous acid, if present, will be reduced to sulphuretted hydrogen by the action of the nascent hydrogen, and a brown or black stain of lead sulphide will appear on the filter paper covering the beaker. If only traces of sulphurous acid are present, the stain may not appear for about 10 minutes.

## The Examination and Analysis of Malt.

The method of preparation and chief characteristics of malt have been outlined above. (See p. 248). As in the case of barley, it requires considerable experience to judge of the quality of a malt by its outward characteristics.

*Sampling.*—See under the Examination and Analysis of Barley.

*Mechanical Tests.*—Tests similar to those enumerated under (*b*) to (*d*) on p. 270, for barley, are applied also to malt.

### Chemical Examination.

*Water.*—This may be determined by drying about 5 grams of the finely powdered malt in a weighing bottle, as described for barley on p. 271, at 105° for not more than 4 hours.

Freshly cured malts may contain from about 1 to 3 per cent. of water, while malts which have been stored for any length of time, may contain from 4 to 6 per cent., or even more. Malts containing more than 6 per cent. of water may usually be regarded as inferior in quality, yielding beers of poor taste and keeping qualities. Pale, or lightly cured malts generally contain slightly more water than dark malts. Malts which are known to have been stored for a long time and which contain less than 3 per cent. of water should be regarded with suspicion, as they may possibly have been subjected to an extra drying.

*Preparation of Extract.*—An important feature in the valuation of malt for brewing purposes is the preparation of an aqueous extract for chemical and physical examination. Great care should be taken in carrying out the following directions, as the analytical results are likely to be influenced by apparently trifling differences in the method of preparing the extract. The directions, given by Weber, include a " saccharification test."

For the preparation of the mash, a 500 c.c. beaker of nickel, aluminium or brass will be required. The clean, dry beaker is first weighed together with a thermometer, and the weight noted. A little over 50 grams of the malt is ground to a fine powder, and exactly 50 grams of the powder weighed out in the beaker. 200 grams of water at 48° to 50° are added, and the beaker is immediately placed in a water bath at 45°, and kept at this temperature for half an hour; the temperature is then raised at the rate of 1° per minute up to 70°, and kept at this point for 1 hour; throughout the whole mashing process, the contents of the beaker should be gently stirred with the thermometer. After the mash has been kept at 70° for 10 minutes, a drop is removed and tested for starch by mixing with a drop of iodine solution on a white tile; if a red or blue coloration is produced, the whole of the starch has not yet been converted into dextrin and maltose, and the test is repeated every 5 minutes until no coloration is obtained with iodine.

The time from the moment at which the temperature of the mash reached 70° to the complete disappearance of the starch is noted (Saccharification Test). With pale, lightly cured malts, of high diastatic value, the time for " saccharification " is usually about 10 to 15 minutes, with intermediate malts, 15 to 20 minutes, and with dark malts, which have somewhat lower diastatic values, owing to the heavy curing, 25 to 30 minutes.

When the saccharification is complete, the material adhering to the sides of the beaker is loosened by means of the thermometer and use of a wash bottle, and the temperature kept at 70° until the hour is up. The beaker is then removed from the water bath, and 200 c.c. of distilled water are added, or correspondingly less if much water was used in loosening the material adhering to the sides of the beaker. The whole is cooled to under 20°, the outside of the beaker wiped dry, and the weight of the contents made up to exactly 450 grams with water, the weight of the empty beaker and thermometer having previously been determined as directed. The contents of the beaker are well mixed and brought on to a dry fluted filter ; the filtrate, or wort, as it is called, may now be used for the determinations of extract, sugar, nitrogen, ash and phosphoric acid, and depth of colour. It is of interest from the point of view of the brewer to note the odour of the wort and whether it filters clear or turbid.

*Determination of Extract.*—The specific gravity of the wort at 17·5° is determined by means of the pyknometer. A float specially designed for the purpose may also be used, though the results obtained by this method are less accurate. The percentage of extract by weight may then be found by reference to the accompanying table.

It now remains to calculate the percentage of extract on the malt itself (air dried) or the anhydrous malt.

Suppose the wort to contain 8·0 per cent. of extract, and the malt to contain 5·0 per cent. of water.

100 parts of wort will then contain 92 parts of water. The weight of mash before filtering was 450 grams, consisting of 400 grams of water, and 50 grams of malt. As the 50 grams of malt contained 2·5 grams of water, the total water in the 450 grams of mash was 402·5 grams. Now in the water, 92 parts of wort correspond

to 8 parts of extract, so in the mash, 402·5 parts of water will correspond to

$$\frac{8 \cdot 0 \times 402 \cdot 5}{92 \cdot 0} = 35 \cdot 0 \text{ parts of extract.}$$

thus, 50 grams of malt yield 35 grams of extract, therefore the malt will yield 70·0 per cent. of extract.

As 100 parts of malt consist of 5 grams of water and 95 grams of anhydrous malt, the anhydrous malt will yield

$$70 \times \frac{100}{95} = 73 \cdot 7 \text{ per cent. of extract.}$$

BALLING'S TABLES FOR MALT EXTRACT. (*Abridged*)

| Sp. Gr. | Per cent. Extract. | | Sp. Gr. | Per cent. Extract. | | Sp. Gr. | Per cent. Extract. | |
|---|---|---|---|---|---|---|---|---|
| | By Weight. | By Volume | | By Weight. | By Volume. | | By Weight. | By Volume. |
| 1·000 | 0·00 | 0·00 | 1·025 | 6·25 | 6·41 | 1·050 | 12·29 | 12·90 |
| 1·001 | 0·25 | 0·25 | 1·026 | 6·49 | 6·66 | 1·051 | 12·52 | 13·15 |
| 1·002 | 0·50 | 0·50 | 1·027 | 6·74 | 6·92 | 1·052 | 12·75 | 13·41 |
| 1·003 | 0·75 | 0·75 | 1·028 | 6·98 | 7·18 | 1·053 | 13·00 | 13·69 |
| 1·004 | 1·00 | 1·00 | 1·029 | 7·25 | 7·46 | 1·054 | 13·25 | 13·97 |
| 1·005 | 1·25 | 1·26 | 1·030 | 7·45 | 7·67 | 1·055 | 13·48 | 14·24 |
| 1·006 | 1·50 | 1·51 | 1·031 | 7·70 | 7·94 | 1·056 | 13·71 | 14·48 |
| 1·007 | 1·75 | 1·76 | 1·032 | 7·95 | 8·20 | 1·057 | 13·95 | 14·75 |
| 1·008 | 2·00 | 2·02 | 1·033 | 8·20 | 8·47 | 1·058 | 14·20 | 15·02 |
| 1·009 | 2·25 | 2·27 | 1·034 | 8·45 | 8·74 | 1·059 | 14·43 | 15·28 |
| 1·010 | 2·50 | 2·52 | 1·035 | 8·68 | 8·98 | 1·060 | 14·67 | 15·55 |
| 1·011 | 2·75 | 2·78 | 1·036 | 8·93 | 9·25 | 1·061 | 14·90 | 15·81 |
| 1·012 | 3·00 | 3·04 | 1·037 | 9·17 | 9·47 | 1·062 | 15·15 | 16·09 |
| 1·013 | 3·25 | 3·29 | 1·038 | 9·41 | 9·77 | 1·063 | 15·37 | 16·34 |
| 1·014 | 3·50 | 3·55 | 1·039 | 9·65 | 10·03 | 1·064 | 15·60 | 16·60 |
| 1·015 | 3·75 | 3·81 | 1·040 | 9·90 | 10·31 | 1·065 | 15·84 | 16·87 |
| 1·016 | 4·00 | 4·06 | 1·041 | 10·15 | 10·57 | 1·066 | 16·07 | 17·13 |
| 1·017 | 4·25 | 4·32 | 1·042 | 10·38 | 10·81 | 1·067 | 16·30 | 17·39 |
| 1·018 | 4·50 | 4·58 | 1·043 | 10·61 | 11·07 | 1·068 | 16·53 | 17·65 |
| 1·019 | 4·75 | 4·84 | 1·044 | 10·85 | 11·33 | 1·069 | 16·77 | 17·93 |
| 1·020 | 5·00 | 5·10 | 1·045 | 11·10 | 11·60 | 1·070 | 17·00 | 18·19 |
| 1·021 | 5·25 | 5·36 | 1·046 | 11·33 | 11·87 | 1·071 | 17·22 | 18·44 |
| 1·022 | 5·50 | 5·62 | 1·047 | 11·59 | 12·13 | 1·072 | 17·45 | 18·71 |
| 1·023 | 5·75 | 5·88 | 1·048 | 11·80 | 12·37 | 1·073 | 17·67 | 18·95 |
| 1·024 | 6·00 | 6·14 | 1·049 | 12·05 | 12·64 | 1·074 | 17·90 | 19·23 |

The yield of extract on the anhydrous malt usually lies between 72 and 80 per cent.

It is of interest to the brewer to know the yield of extract obtainable from malt, as this, together with the added brewing sugar[1] (invert sugar or glucose) constitutes the fermentable material used in the brewing of beer. The yield is usually stated in lbs. per quarter (28 lbs.).

*Sugar.*—A portion of the wort, obtained as described above, is diluted to 10 times its volume, and the sugar determined as described on p. 140. (See also p. 242.) The copper oxide obtained may be converted to maltose by reference to the table on p. 243.

In order to find the percentage of sugar in the extract, the percentage of extract *by volume* in the wort is found by reference to the table on p. 276. Having determined the sugar in a given volume of wort, the sugar in the extract corresponding to this volume of wort is easily calculated, and hence the percentage of sugar in the extract.

Subtracting the percentage of sugar in the extract from 100, the percentage of matter other than sugar in the extract is found.

According to Weber, the ratio of the sugar to extract less sugar, varies from 1 : 0·4 or 0·5 in pale (Pilsner) malts, to 1 : 0·6 or 0·7 in dark (Munich) malts.

*Nitrogen.*—25 c.c. of the wort, obtained as described above, are evaporated to a syrup, and the nitrogen, and hence the proteins, determined in the latter by the Kjeldahl process, as described on p. 22. As in the case of malt, the factor for converting nitrogen into proteins is 6·25.

The percentage of nitrogen, calculated on the extract, varies from 0·5 to 0·8, and the proteins from 3 to 5.

[1] Brewer's "glucose" contains, besides glucose, maltose and dextrin.

The nitrogen may also be determined direct, on the finely ground malt.

Although both in barley and malt the whole of the nitrogen is not present as proteins, the determination of nitrogen is nevertheless of value when used comparatively especially in its bearing on the physiology of the fermentation process.

*Ash.*—50 c.c. of the wort are evaporated to dryness in a weighed platinum dish, and the residue incinerated. (See p. 259.)

The content of ash in the extract (refer to tables as explained above for sugar) varies from 1·4 to 1·9 per cent.

*Acidity of Malt.*—100 grams of finely powdered malt are well mixed with 400 c.c. of 20 per cent. alcohol, and allowed to stand for 6 hours, the mixture being shaken from time to time. The mixture is then filtered, and 100 c.c. of the filtrate are titrated with decinormal sodium hydroxide or baryta solution, until a drop brought on to a piece of sensitive blue litmus paper no longer produces a red coloration. The number of cubic centimetres of decinormal alkali used is calculated to lactic acid by multiplying it by 0·009.

The percentage of acid, calculated as lactic acid, in malt, varies from 0·15 to 0·4.

*Diastatic Value.*—The determination of the diastatic value of malt and malt extract is described on p. 249.

*Colour of the Wort.*—The depth of colour of the wort, obtained as described above, is determined by means of specially designed colorimeters, comparison being made with the colour of iodine solutions of known strength.

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# CHAPTER VIII

## PRESERVATIVES AND ARTIFICIAL COLOURING MATTERS IN FOODS

### PART I.—PRESERVATIVES.

#### INTRODUCTORY.

ALL foodstuffs are liable to decomposition and decay through the agency of micro-organisms, and if they are to be kept for any length of time in a state fit for human consumption, it is sometimes necessary to adopt some means for their preservation, by which the micro-organisms which they contain may either be destroyed or temporarily rendered sufficiently inactive to prevent them from appreciably affecting the food.

The method of heat sterilisation and subsequent preservation in hermetically closed vessels, as practised in the canning industry, has for its object the destruction of the micro-organisms by heat (see Chapter VI.) and the protection of the food from further contamination until it reaches the consumer. Preservation by cold storage is based on the fact that micro-organisms become inactive at low temperatures, while the treatment of the food with wood smoke, salt or other chemicals has a similar effect, *i.e.*, the temporary checking of the activity of the micro-organisms, without, however, destroying them.

Heat sterilisation, if efficiently carried out, is naturally more thorough in its effects than the other methods just mentioned, though it has a real disadvantage when applied to many foodstuffs owing to the partial decomposition suffered by proteins and carbohydrates under the influence of heat. (See Chapter VI., the Heat Sterilisation and Pasteurising of Milk, also Condensed Milk.)

In cases when, for this and other reasons, the food cannot be completely sterilised by heat, recourse may also be had to cold storage and sometimes also the addition of chemical preservatives. Cold storage and addition of preservatives may also be practised simultaneously. The merits and disadvantages of the latter method will be discussed below ; it may, however, be pointed out here that, generally speaking, it would probably be in the best interest of the consumer if the method of cold storage were employed in preference to the addition of preservatives, wherever possible.

In the present chapter we are concerned with the method of preserving by the addition of certain chemicals with the object of inhibiting the growth and development of micro-organisms in the food ; among the substances which have been used in this capacity, the following may be mentioned : Common salt, boric acid and borax, sodium fluoride, sulphites and sulphurous acid, benzoic acid and benzoates, salicylic acid and salicylates, formaldehyde, $\beta$ naphthol, abrastol or asaprol (the calcium salt of $\beta$ naphthol sulphonic acid), hydrogen peroxide, saccharin, formic acid and formates. As regards the advisability of permitting such substances to be added to foods, two main questions come into consideration :—

Firstly, the question as to whether the substance added is injurious to health, even in the minutest proportions, or has an undesirable effect on the food with which it comes into contact, and if not, the maximum proportion in which it can be added without prejudice to the purchaser. While the use of such a preservative as common salt has long been recognised and sanctioned in all countries, considerable diversity of opinion still exists as to the advisability of permitting the use of certain preservatives, such as borax, boric acid or benzoic acid in small quantities ; other preservatives, such as sodium fluoride and formaldehyde, are generally looked on as distinctly injurious to health.

Secondly, there is the question as to whether, with proper organisation, care and cleanliness, it is possible to supply a given article of food to the consumer in a

fresh and pure state, without the addition of preservatives. If this be the case, then the use of preservatives must obviously be looked on as decidedly objectionable, as it may often be practised in order to temporarily mask uncleanliness in treatment. This point will be further discussed below, in dealing with the subject of preservatives in milk.

The law of the United Kingdom does not definitely prohibit the use of any given substance as a preservative for foods, nor does it actually set any definite limit as to the proportion in which any given preservative may be used.

Section 3 of the Sale of Foods and Drugs Act of 1875 provides that "No person shall mix, colour, stain, or powder . . . any article of food with any ingredient or material so as to render the article injurious to health, . . . under a penalty in each case not exceeding fifty pounds for the first offence; every offence, after conviction for a first offence, shall be a misdemeanour, for which the person, on conviction, shall be imprisoned for a period not exceeding six months with hard labour."

Very few prosecutions have been instituted under this section, and practically all prosecutions are instituted under section 6 of the same Act, which is to the following effect :—

"No person shall sell to the prejudice of the purchaser any article of food or any drug which is not of the nature, substance, and quality of the article demanded by such purchaser, under a penalty of twenty pounds. . . ." Exceptions are made in the case of foreign matter not injurious to health, necessarily or unavoidably added in the preparation of the food or drug, and not with the object of fraudulently increasing its bulk or weight, or concealing its inferior quality; also in the case of proprietary or patent medicines, supplied in a state required by the specification of the patent.

The purchaser is not held to be prejudiced if notice was given him at the time of the sale that the article sold was not of the nature, substance and quality of the article demanded; further, in order to show that the article was sold to the prejudice of the purchaser, it is

not necessary to show that he has sustained actual prejudice or damage.

Questions as to whether the purchaser shall be held to have been prejudiced by the addition of material injurious to health to the article supplied, or otherwise, are usually decided with reference to the opinions and recommendations of the Medical Officers of Health and other experts. With the exception of the Public Health (Milk and Cream) Regulations of 1912, referred to below under the heading of Preservatives in Milk, Cream, Butter and Margarine, no further legislation has resulted from such recommendations. This matter will be more fully dealt with below, under the various headings.

In the United States the law forbids the sale of food containing poisonous or deleterious substances which may render the food injurious to health, but does not definitely prohibit or limit the use of any given preservative. Some preservatives, such as boric and salicylic acids, and formaldehyde, are, however, held to be injurious to health, and prosecutions have been successfully maintained against them ; the matter is at present under investigation.

In France, Germany, Austria-Hungary and Holland, the law is, generally speaking, more explicit and stringent with regard to the use of preservatives ; either certain preservatives may be totally prohibited, or the use of preservatives in certain foods may be forbidden.

## Preservatives in Milk, Cream, Butter and Margarine.

The provisions of the Public Health (Milk and Cream) Regulations of 1912 are, briefly, as follows : The addition of preservative substance of any kind to milk intended for sale for human consumption is absolutely prohibited ; also the sale, or offering, exposing or keeping for sale, of milk containing any preservative.

The addition of preservatives to cream which contains less than 35 per cent. of fat is prohibited, and the only preservatives which may be added to cream which contains more than 35 per cent. of fat are boric acid and

borax, or mixtures of these, and hydrogen peroxide. Cream containing preservative must be described as "Preserved Cream," on a label on the vessel in which it is sold, and in all advertisements, price lists, etc., used in connection with its sale; if it contains boric acid or borax, the amount of these substances, calculated as boric acid ($H_3BO_3$) must be accurately stated on the label as not exceeding a certain limit.

The main reasons why preservatives should be excluded from milk are stated in the circular letter of the Local Government Board, dated July 11th, 1906, as follows: "Under the influence of these preservatives,[1] milk may be exposed without sensible injury to conditions which would otherwise render it unsaleable. It may remain sweet to taste and smell, and yet have incorporated disease germs of various kinds, whereof the activity may be suspended for a time by the action of the preservative, but may be resumed again after the milk has been digested. The Committee, after hearing evidence from milk traders, concluded that the addition of preservatives to milk is not necessary for the purposes of the milk trade . . . and the Committee recommended that no preservatives should be added to milk." A further important reason for the above recommendation was the fact that milk is largely consumed by children and invalids, *i.e.*, individuals who would be especially susceptible to the harmful influence of any preservative.

The addition of preservatives to milk is prohibited in most other countries.

With regard to cream, no definite limit has been set on the amount of boric acid which may be used for its preservation. In his report to the Local Government Board on the Use of Preservatives in Cream, 1909, Dr. J. M. Hamill recommended that the maximum amount of boric acid ($H_3BO_3$) should be 0·4 per cent. from May to October, inclusive, and 0·25 per cent. during the rest of the year; for the present, however, it is probable that prosecution under the Sale of Foods and Drugs Act would not succeed for less than 0·5 per cent.

[1] The evidence on which these observations were based was chiefly in connection with boric acid and formaldehyde.

of boric acid. In the report mentioned above, it is pointed out that as cream is used to a considerable extent as food for children and invalids, individuals specially sensitive to boric acid, the declaration of the presence of this substance should be made obligatory, in order that it may be avoided by those who object to it.

In France and most of the United States of America, the use of preservatives in cream is prohibited by law; in Germany, persons selling preserved cream are liable to proceedings under the Nahrungsmittelgesetz of 1879.

As regards butter and margarine, it was recommended in the circular letter of the Local Government Board referred to above, that the only preservative allowed in these foods should be boric acid or borax, in proportions not exceeding 0·5 per cent., expressed as ($H_3BO_3$). It is probable that for the purposes of the Sale of Foods and Drugs Act, the limit would be placed at 0·5 per cent. of boric acid; thus, a prosecution for 51 grains per pound[1] of boric acid in margarine succeeded, while a conviction for 25 grains per pound of boric acid in butter was quashed at the Quarter Sessions. It is, however, doubtful whether the use of any preservative other than boric acid (or salt) would, in itself, be considered an offence.

In Germany, Holland, and some other countries, preservatives, except salt, are prohibited in butter and margarine.

Before starting on the description of the methods for the detection of preservatives in milk, cream, butter and margarine, it may be mentioned that milk is rarely treated with preservatives; on account of the importance of excluding preservatives from milk, however, methods for detecting most of the commoner preservatives in this article of food are given below.

*Sodium Carbonate or Bicarbonate in Milk.*—These substances have no antiseptic action, but are added in order to neutralise the lactic acid produced in the souring of the milk (see Chapter VI.), and thus to prevent coagulation. The growth of the bacteria is not impeded.

According to Padé, the ash of 10 c.c. of genuine milk

[1] 35 grains per pound = 0·5 per cent.

should require only 1 drop of decinormal acid for neutralisation (indicator methyl orange); if an alkali carbonate has been added, more acid will be required for neutralisation of the ash.

The estimation of added carbonate by this method may be interfered with owing to the conversion of some of the carbonate to phosphate during the incineration; in order to allow for this, it is recommended that the soluble phosphate should be determined in the ash, recalculated to sodium carbonate, and added to the amount of carbonate already found by titration.

Soxhlet and Scheibe estimate the carbon dioxide in the ash of the milk; they state that ash from genuine milk should not yield over 2 per cent. of carbon dioxide.

Sodium carbonate has been known to have been added to milk in the proportion of 1 part of the anhydrous salt per litre.

*Detection of Boric Acid (or Borax).* (*a*) *In Milk or Cream.*—10 c.c. of the milk or cream are made alkaline with milk of lime, evaporated to dryness, and the residue ignited until all organic matter is destroyed and converted into carbon. The ash is dissolved in the smallest possible quantity of dilute hydrochloric acid, and the solution filtered from the carbonaceous residue. The filtrate is evaporated to dryness in order to expel completely the excess of acid; for this purpose, the residue may, if necessary, be treated with a further quantity of water, and the solution again evaporated to dryness. The residue is then moistened with a little very dilute hydrochloric acid, and a little tincture of turmeric is stirred into the crystalline mass. If the least trace of boric acid be present, a cherry-red coloration will result. In this way the presence of as little as 0·001 to 0·002 per cent. of boric acid in milk or cream may be shown. It

should be noted that concentrated hydrochloric acid also produces a cherry-red coloration with turmeric, but in the absence of boric acid, this coloration would be discharged on dilution.

If preferred, the ash may also be tested for boric acid by the well-known green flame reaction, as described below on p. 298.

(*b*) *In Butter or Margarine.*—Boric acid may be detected by examining, as described above, the aqueous serum which collects beneath the fat when the butter or margarine is melted and allowed to stand in a cylindrical vessel at about 60° for an hour or two. Boric acid may also be tested for in the water soluble portion of the non-fatty solids, obtained as described in Chapter VI., p. 230.

*The Estimation of Boric Acid.* (*a*) *In Milk.*—A known quantity of milk, say 100 grams, is made alkaline with milk of lime, evaporated to dryness and incinerated as described under the determination of ash in milk in Chapter VI., p. 208.

The residue is dissolved in a convenient quantity of water to which a little hydrochloric acid has been added, and the boric acid determined in the solution as described below, under the next heading.

(*b*) *In Butter, Margarine and Cream.*—50 grams of the sample are warmed and well shaken with 50 c.c. of water. After cooling and allowing the layers to separate, most of the aqueous layer is syphoned off, 50 c.c. thereof placed in a 100 c.c. measuring flask and heated in boiling water, while decinormal sulphuric acid is added in small quantities from time to time, until the casein separates as a flocculent precipitate. The solution is then cooled, made up to 100 c.c. and filtered through a dry filter; 50 c.c. of the filtrate may then be measured off for the

boric acid titration, the rest being preserved for the salt estimation. The method adopted for the estimation of the boric acid depends on the fact that this substance may be titrated with sodium hydroxide solution and phenol phthalein as indicator, in presence of glycerol. The solution for the titration is first made neutral to methyl orange by adding a slight excess of decinormal sodium hydroxide solution, and then decinormal sulphuric acid, till a pink tint just appears; glycerol previously made neutral to phenol phthalein with sodium hydroxide is then added in sufficient amount to make up about one-third of the bulk of the liquid, which is then titrated with decinormal sodium hydroxide solution in presence of a few drops of phenol phthalein solution, till a pink tint appears. 1 c.c. of decinormal alkali corresponds to 0·0062 gram of boric acid ($H_3BO_3$), 1 molecule of boric acid neutralising 1 molecule of sodium hydroxide, under the conditions of the titration.

In calculating the amount of boric acid in the sample, the amount of water in the latter must be allowed for. Thus, if the butter contained 14 per cent. of water, the total volume of the aqueous layer would be 57 c.c., of which 50 c.c. were diluted to 100 c.c., of which, again, 50 c.c. were taken for the titration. The estimation of water in butter and margarine has already been described in Chapter III., p. 85. The amount of water in cream may be arrived at with sufficient accuracy for the present purpose, by subtracting the percentage of fat from 100. The estimation of fat in cream is described in Chapter VI., p. 197.

*The Estimation of Salt in Butter and Margarine.*—10 c.c. of the filtered slightly acid liquid as used for the boric acid titration are diluted with distilled water to about 50 c.c., and titrated with decinormal silver nitrate

solution, with a few drops of potassium chromate as indicator, in the usual way. The calculation of the percentage of salt in the sample is made on the same lines as indicated above for boric acid.

*Detection of Salicylic and Benzoic Acids.*—These substances may be added as such, or in the form of their sodium salts. In most countries their use as preservatives for butter or margarine is not allowed, and in France they are definitely prohibited by law, in all foods.

(*a*) *In Milk.*—Girard recommends the following process for the detection of salicylic acid in milk ; it may also be applied for the detection of benzoic acid : 100 c.c. of the milk are diluted with 100 c.c. of water at 60°, treated with 8 drops of acetic acid and 8 drops of a saturated solution of mercuric nitrate, shaken and filtered. The acid filtrate, which has thus been freed from fat and proteins, is extracted with ether, which will take up the salicylic or benzoic acid. The ethereal layer is separated off, filtered through a dry filter and allowed to evaporate spontaneously in a dish ; salicylic or benzoic acid, if present, will then be obtained as a white crystalline powder. For identification, the crystals may be sublimed on to a watch glass and tested for their melting point ; salicylic acid melts at 155° to 156°, and benzoic acid at 121°. The following reactions may also be used for the identification of these acids : In neutral aqueous or alcoholic solution, salicylic acid gives a fine violet coloration on the addition of a drop or two of neutral ferric chloride solution, and benzoic acid gives a buff-coloured precipitate with the same reagent in neutral aqueous solution. If an aqueous solution of benzoic acid is warmed for 5 to 10 minutes on the water bath with a few cubic centimetres of a 0·5 per cent. solution of hydrogen peroxide, the benzoic acid is partially con-

verted into salicylic acid, which may be recognised by the reaction just described. A delicate reaction for the detection of benzoic acid in the absence of salicylic acid is given under the next heading. (See also p. 306.)

(*b*) *In Butter and Margarine.*—The following method has been devised by Robin for the detection of benzoic acid; it may also be adapted for the detection of salicylic acid: 25 grams of the melted butter or margarine are shaken in a separating funnel with 50 c.c. of a 1 per cent. solution of sodium bicarbonate, 15 c.c. of alcohol being added in order to facilitate the separation of the fat from the aqueous liquid. After shaking with a rotary motion, so as to avoid the formation of a troublesome emulsion, and allowing the layers to separate, the aqueous alcoholic liquid is run off, treated with 7 to 8 drops of sulphuric acid, heated to boiling, shaken with a little fuller's earth (in order to facilitate the separation of the proteins), and filtered through a wet filter. The cooled filtrate is shaken out with 40 c.c. of ether, and the ethereal extract, containing the benzoic or salicylic acid, is separated off and shaken with 20 c.c. of water and 5 c.c. of alcohol to remove excess of mineral acid, and then with 20 c.c. of a 1 per cent. solution of sodium bicarbonate and 5 c.c. of alcohol. The alkaline solution, which will contain the benzoic or salicylic acids as sodium salts, is run into a small dish and evaporated to dryness on the water bath. A small portion of the residue may now be tested for salicylic acid by dissolving in water and adding neutral ferric chloride to the neutral solution; if salicylic acid be absent, the bulk of the residue may be tested for benzoic acid by the following delicate reaction: Add 5 c.c. of concentrated sulphuric acid and 10 drops of fuming nitric acid, and heat carefully until white fumes are given off. Pour the resulting

mixture, which should be colourless or light yellow, into 50 c.c. of water, and add sufficient concentrated ammonia solution to give a decidedly alkaline reaction. After cooling, add ammonium sulphide solution drop by drop ; if benzoic acid was present in the sample, an orange yellow coloration will be produced, depending on the formation of the ammonium salt of an amido nitro benzoic acid. By this method, the presence of 0·05 per cent. of benzoic acid in the sample may easily be detected. (See also p. 306.)

*The Detection of Formaldehyde in Milk.*—This preservative is generally looked on as poisonous ; a further objection to its use is that it enters into chemical combination with proteins. It should be tested for in milk before the sample is too old, as it (the formaldehyde) disappears in time.

The best method for the detection of formaldehyde in milk is to add 1 c.c. of dilute sulphuric acid (1 part acid to 3 parts water) to 100 c.c. of the sample and to distil until the distillate measures 20 c.c. 10 c.c. of the distillate are tested with Schiff's reagent, *i.e.*, a solution of magenta which has been bleached by adding just the requisite quantity of sulphurous acid. If, after 5 to 10 minutes, an intense carmine red coloration is formed which, on the addition of 2 c.c. of hydrochloric acid turns to a violet blue, the sample contains formaldehyde.

Hehner's test for formaldehyde in milk, as modified by Richmond and Bosely, is as follows : The milk is diluted with an equal bulk of water, and 94 per cent. sulphuric acid containing a trace of a ferric salt is added in such a way that it will form a layer under the milk ; in the presence of formaldehyde, a violet coloration is formed at the junction of the layers ; in the absence of formalde-

hyde, only a faint, greenish coloration will be observed. This test, which is of extreme delicacy, is only applicable to milk. Further tests for formaldehyde, applicable to other foodstuffs, are given below.

In addition to the objections to the use of formaldehyde in milk, already mentioned, it may be pointed out that this preservative has been shown by Sommerfeld to have a more pronounced action on the relatively harmless organisms, *e.g.*, the lactic acid producing bacteria, than on the pathogenic and putrefactive organisms which may occur in milk. This was found to be the case when formaldehyde was added in the proportion of 1 to 10,000. It is obvious that if the activity of the harmless bacteria is impaired to a greater degree than that of the more injurious organisms, the latter will be able to develop more freely and render the milk unfit for use. (Compare Chapter VI., p. 215.)

*The Detection of Hydrogen Peroxide in Milk.*—Like formaldehyde, this preservative is gradually decomposed by milk, and disappears after a time. The hydrogen peroxide is decomposed into water and oxygen by a catalytic action, the nascent oxygen having a bactericidal action. This principle is utilised in Budde's process for sterilising milk. Hydrogen peroxide is usually added in the proportion of about 0·05 per cent.; sometimes the milk is heated with the hydrogen peroxide in closed vessels to 50° for 8 to 10 hours, after which it is supposed to be sterile. It has, however, been shown that the hydrogen peroxide does not destroy all the pathogenic organisms when used in the concentration mentioned, while if the amount necessary for complete sterilisation, *i.e.*, 0·4 per cent., is added, a bitter taste is produced, probably owing to the oxidation of the olein of the milk fat.

Hydrogen peroxide may be detected by adding to about 10 c.c. of the milk a few drops of a recently prepared solution of potassium iodide and starch, and then a very small quantity of dilute ferrous sulphate

solution; in the presence of hydrogen peroxide, a blue coloration will be developed. The reaction is extremely delicate.

*The Detection of Sodium Fluoride.*—The milk, cream or aqueous serum from butter or margarine is made distinctly alkaline with milk of lime, evaporated to dryness and incinerated. The ash is placed in a platinum dish, moistened with water, and 5 c.c. of concentrated sulphuric acid are added. The dish is then covered with a watch glass which has been coated on the under side with paraffin wax, the latter having been scraped off in a few places. Gentle heat is applied, care being taken not to melt the paraffin. If the exposed parts of the glass become etched in the course of about half an hour, the presence of fluoride may be inferred. In the presence of compounds of boron, the test must be modified as described under the next heading.

*The Detection of Fluoride in presence of Boron Compounds in Butter and Margarine.*—The test for fluoride is complicated by the presence of boric acid or borax, owing to the formation of fluoboric acid, which has no etching effect on glass. As many butters and margarines contain boric acid or borax, Otto and C. W. Hehner have devised the following test: 50 grams of the sample are melted and mixed with 50 c.c. of hot water; the aqueous layer is separated from the fat in a separating funnel and made alkaline with sodium carbonate. After adding an excess of calcium chloride, the liquid is evaporated to dryness; the residue is incinerated, and the ash extracted with dilute acetic acid, transferring it to a filter and washing with the acid. The boron compounds are thus dissolved, while the calcium fluoride remains on the filter. The filter with the insoluble ash is transferred to a platinum dish, dried and

incinerated. The ash is then tested for fluoride as described above.

### Preservatives in Meat, Wine and other Foods.

Most of the methods for the identification and estimation of preservatives given above may be applied in the case of other foods, the method of extracting the preservative being varied to suit any particular case. Solid or semi-solid foods, such as meat or sausages, are usually comminuted and extracted with water; the filtered aqueous extract may then be acidified and extracted with ether or chloroform, when such preservatives as benzoic and salicylic acids, or saccharin will pass into the organic solvent, while fluorides, boric acid, etc., will remain in solution in the aqueous layer. In some cases it may be convenient to render the aqueous extract alkaline and to evaporate it to a small bulk before acidifying and extracting with ether. Liquids may be treated in the same way as the aqueous extract from solid foods. Another general method is to steam distil the material in presence of phosphoric acid, when benzoic and salicylic acids, etc., and sulphurous acid, from sulphites, will pass over with the distillate.

As examples of the methods generally in use, the detection, and in some cases also the estimation, of some of the commoner preservatives in meat and wine will be described. Besides common salt, nitre, sugar, wood smoke, vinegar and spices, the commonest preservatives used in meat and meat food products are formaldehyde, boric acid or borax, and sulphites (usually sodium or calcium bisulphites). The use of the latter preservatives in meat is forbidden by law in Germany and the United States. American packers may, however, under the direction of the foreign purchaser or his agent, add preservatives to meat and meat-food products intended for export, in proportions which do not conflict with the

laws of the foreign country to which they are to be exported. As has already been pointed out, the law of the United Kingdom contains no definite prohibitions for the use of preservatives in foods, except in the case of milk and cream. It may be mentioned that a conviction for 29 grains of boric acid per pound in sausages was quashed under section 6 of the Food and Drugs Act of 1875, while prosecutions have succeeded for 40 grains of boric acid per pound, and larger quantities, in similar foodstuffs. Formaldehyde is generally held to be harmful; it is used for fumigating meat intended for long transit, and is a very efficient preservative, but has a harmful effect on the digestion.

The Departmental Committee on Preservatives and Colouring Matters in Foods, 1901, recommended that the use of formaldehyde or its preparations in foods or drinks be absolutely prohibited. In a report to the Local Government Board, 1909, Dr. Buchanan recommended that meat traders and importers should consider the practicability of limiting the use of formaldehyde to the adequate disinfection of the holds in which the meat is to be conveyed, before it is introduced. In a report to the Local Government Board on Preservatives in Meat Foods packed in Cans or Glasses, 1908, Dr. MacFadden points out that a considerable proportion of the samples of canned meat foods, both of British and American manufacture, examined by different analysts, contained either boron or sulphite preservatives. In reviewing he recommends that "steps should be taken to secure that specified chemical preservatives should not be used in the preparation of canned meats intended for use in this country," and that "in any schedule of prohibited preservatives, boron compounds, sulphites and preparations of sulphurous acid, benzoic acid and formalin should be included."

The chief preservative used in wines, beers and other beverages, is salicylic acid. The Departmental Committee on Preservatives and Colouring Matters in Foods, 1901, recommended that this preservative should not be used in a greater proportion than 1 grain per pint in liquid food, and 1 grain per pound in solid food. Quite a

number of prosecutions have been successfully maintained against salicylic acid, though the results show but little uniformity; thus cases may be cited in which prosecutions for 13 grains per pint in ginger wine failed, and 7·2 grains per pint in similar material procured conviction. A prosecution for 1·7 grains per lb. in jam failed, while 2·67 grains per lb. procured conviction. Besides salicylic and benzoic acids, beverages may be preserved with sulphites, fluorides and boric acid. Saccharin is sometimes added to wines and sweet beverages in order to reduce the amount of sugar and lessen the fermentation; it is said to conceal inferior quality, and also to have a harmful effect on digestion. Fruit juices, jams, etc., may be preserved with benzoic, salicylic, boric and formic acids.

In Germany, practically all the preservatives mentioned above (and in the case of acids, also their salts) are forbidden by law in meat and wine. Sulphurous acid and sulphites, not being considered poisonous, are not excluded from wine. They are, however, prohibited in meat, as sulphurous acid tends to restore the colour of bad meat. In France, most of the common preservatives are forbidden in wine, while the use of salicylic acid, benzoic acid, and their salts, and formaldehyde as preservatives is forbidden altogether.

*Detection and Estimation of Formaldehyde in Meat.*—The reaction given above for the detection of formaldehyde in milk, depending on the formation of a violet coloration in the presence of proteins, mineral acid and an oxidising agent, cannot be applied here, as meat gives a violet colour on warming with mineral acid in the absence of the aldehyde. The following method has been devised by Dr. Schryver (Report to Local Government Board on the Application of Formaldehyde to Meat, 1909) for the detection of formaldehyde, polymerised formaldehyde or formaldehyde which has entered into combination with other substances, *i.e.*, the proteins of the meat: 10 grams of the minced meat are heated for

5 minutes on a boiling water bath, with water to every 10 c.c. of which have been added 2 c.c. of a 1 per cent. solution of phenyl hydrazine hydrochloride. The quantity of liquid is varied according to the amount of formaldehyde present. In most cases where the amount of formaldehyde is 1 part in 50,000 or less, 10 c.c. of water and 2 c.c. of phenyl hydrazine solution are employed. Where the concentrations are higher, larger quantities of the liquid must be used. Thus, where the concentration of the aldehyde in the meat reaches 1 part in 5,000, 10 grams of meat are heated with 100 c.c. of water and 20 c.c. of 1 per cent. phenyl hydrazine hydrochloride solution. After heating, the liquid is cooled and filtered from the coagulum through a loose plug of cotton wool. To 12 c.c. of the filtrate are added 1 c.c. of a 5 per cent. solution of potassium ferricyanide and 4 c.c. of concentrated hydrochloric acid for each 12 c.c. of water and phenyl hydrazine reagent employed in the test. In the presence of formaldehyde, a brilliant fuschine-like colour is developed, which reaches its full intensity after a few minutes' standing, and keeps without marked deterioration for several hours. By comparison of the colour with standard solutions containing known amounts of formaldehyde, the amount of formaldehyde in the meat sample can be ascertained.

*Detection and Estimation of Boric Acid* (*or Borax*). (*a*) *In Meat.*—The following is the German official method for meat inspection: 50 grams of the comminuted meat are triturated with 50 c.c. of water, to which has been added 0·2 per cent. of concentrated hydrochloric acid (specific gravity 1·124). The mixture is allowed to stand in a beaker for half an hour, after which it is heated on a boiling water bath for half an hour, with occasional stirring, the beaker being covered with a watch glass.

The warm mass is pressed in muslin, and the liquid extract poured through a moist filter. The filtrate is made faintly alkaline to phenol phthalein by the addition of decinormal sodium hydroxide solution, and evaporated to 25 c.c. 5 c.c. of the liquid thus obtained are acidified, filtered and tested with turmeric paper as follows :—

A strip of turmeric paper 8 cm. long and 1 cm. wide is wetted half its length with the acid liquid and dried on a watch glass at 60° to 70°. If no change is observed on the part which was wetted, then boric acid is absent. If a red or orange-red colour is produced, a little 2 per cent. solution of sodium carbonate (anhydrous) should be added ; if a reddish brown spot is produced, which does not differ from that got with pure turmeric paper and sodium carbonate, then boric acid is absent. If, however, the sodium carbonate solution produces a blue spot, then boric acid is present. If a bluish violet coloration is produced, or the indications obtained are in any way doubtful, the flame test should be applied, the official directions for which are as follows :—

5 c.c. of the concentrated alkaline solution, obtained as described above, are evaporated to dryness and incinerated in a platinum dish. The latter process may be greatly facilitated by extracting the charred mass with 20 c.c. of water, then burning off the residual coal, and finally returning the aqueous extract to the dish, evaporating to dryness and heating the residue to 120°. The ash is well mixed with 5 c.c. of methyl alcohol and 0·5 c.c. of concentrated sulphuric acid, and the whole is transferred to a 100 c.c. Erlenmeyer flask with the aid of a further quantity of 5 c.c. of methyl alcohol. The flask is closed with a cork, and shaken at frequent intervals during half an hour, after which all the alcohol is distilled off, heating the flask in a water bath at 80° to 85°.

The distillate is introduced into a glass cylinder or test tube of about 40 c.c. capacity, about 6 cm. high, and fitted with a cork carrying two glass tubes bent at right angles, one of which passes to the bottom of the vessel, and the other just through the cork. A current of hydrogen is passed through the liquid, and ignited as it emerges from the shorter tube ; if a green-edged flame is produced then boric acid is present.

*Estimation of Boric Acid.*—This may be carried out by evaporating a definite proportion of the concentrated alkaline liquid used for the above tests to dryness, incinerating as described under the green-flame test, dissolving the ash in water and titrating the liquid previously neutralised to methyl orange with decinormal sodium hydroxide solution in presence of glycerol and phenol phthalein, as described on p. 288.

(*b*) *In Wine, Fruit Juices, Jams, etc.*—The following method is due to Allen and Tankard : 100 c.c. of the liquid are evaporated to dryness with 10 c.c. of a 10 per cent. solution of calcium chloride. In the case of solid or semi-solid material, such as jams, mincemeat, etc., the mass should be broken up and the calcium chloride solution well mixed with it. The residue is incinerated by first charring, then extracting the mass with 150 c.c. of water, and filtering the aqueous extract from the coal, which is burnt off by itself. The residue thus obtained is boiled with a second portion of 150 c.c. of water, allowed to stand for 12 hours and filtered cold. The filtered liquid is united with that previously obtained from the charred mass, and the boric acid in solution estimated by titration as described on p. 288. The incinerated residue may be extracted with a further 150 c.c. of water, and the filtrate thus obtained titrated for boric acid, to make sure that this constituent has been

completely extracted. The qualitative tests for boric acid may be carried out as described under the preceding heading (Detection of Boric Acid in Meat) on a portion of the aqueous extract previously made alkaline, and concentrated or evaporated to dryness as the case may require.

*Detection and Estimation of Sulphurous Acid or Sulphites in Meat, Wine, etc.*—The following are the German official methods for the detection and estimation of sulphurous acid and sulphites in meat and wine ; they may also be applied to other materials, such as jams, cider, beer, etc. :—

The qualitative test is carried out as follows with meat : 30 grams of the comminuted meat are rapidly mixed with 5 c.c. of a 25 per cent. solution of phosphoric acid in a 100 c.c. Erlenmeyer flask. The latter is closed with a cork in which a slit has been cut, so that a piece of potassium iodate and starch paper may be suspended from it. The test paper should be freshly prepared by soaking filter paper in a mixture in equal parts of 1 per cent. solutions of potassium iodate and starch, drying at a gentle heat and cutting into strips of convenient size. A strip of this paper is suspended so that the end is about 1 cm. above the meat, and 1 cm. of the lower portion is moistened with water. If in the course of 10 minutes no blue colour appears (usually seen at the junction of the wet and dry parts of the paper), the cork is loosened and the flask is placed on the water bath, warmed, then closed with the cork and allowed to cool ; if no colour is observed on the test paper after half an hour, it may be assumed that the meat is free from sulphurous acid or sulphites.

The method recommended for the estimation is as follows : 30 grams of the comminuted meat, or 100 c.c. of

wine, are mixed with sufficient sodium carbonate solution to render the whole alkaline, in a 500 c.c. round-bottomed, long-necked flask, the volume of liquid being made up to about 150 c.c. After standing for 1 hour, the flask is connected up as for a steam distillation, on the one side with an inlet tube passing well below the surface of the contents, and on the other side with a Liebig condenser which is connected at the other end by means of an adapter, with a U tube having 3 bulbs (Peligot tube), which must be capable of holding 150 c.c. of liquid while gas is being passed through it. A stream of carbon dioxide, entering through the inlet tube in the flask, is passed through the whole apparatus; when all the air has been displaced, the Peligot tube is charged with 50 c.c. of a solution prepared by dissolving 7·5 grams of potassium iodide and 5 grams of iodine in 1 litre of water (pure materials being used, so that the solution is free from sulphates), and 10 c.c. of a 25 per cent. solution of phosphoric acid are added to the contents of the flask, the cork being removed and replaced as quickly as possible; the current of carbon dioxide is maintained throughout. After connecting up the apparatus as before, about half of the liquid is distilled off, still maintaining the current of carbon dioxide. All the sulphurous acid will now have been driven over into the Peligot tube, where it will be oxidised to sulphuric acid by the iodine solution, which should remain brown throughout, showing an excess of iodine to be present. The contents of the Peligot tube and rinsings are transferred to a beaker, hydrochloric acid and barium chloride are added, the mixture boiled, the barium sulphate being precipitated, collected, washed and weighed as in an ordinary sulphate determination. The barium sulphate may then be calculated to sulphur dioxide or sulphurous acid. As

already mentioned, the above methods may be applied or adapted to materials other than wine or meat. Some analysts use a definite volume of iodine solution of known strength, determined by titration with standard sodium thiosulphate solution, and estimate the iodine which has been used up in the oxidation of the sulphurous acid by a second titration with thiosulphate solution. The latter method is somewhat more expeditious than the one given above.

*Detection of Fluorides.* (*a*) *In Meat.*—The German official method is as follows: 25 grams of the minced meat are thoroughly mixed with an excess of milk of lime in a platinum dish, dried and incinerated. The residue is treated with 3 drops of water and 1 drop of concentrated sulphuric acid, the etching test for hydrofluoric acid being applied in the usual way, as described on p. 293.

(*b*) *In Wine.*—Vandam recommends the following method: To 100 c.c. of the sample in a measuring cylinder are added 0·5 to 1 c.c. of a 20 per cent. sodium sulphate solution and 10 c.c. of a 10 per cent. barium acetate solution; after shaking well, the mixture is allowed to stand overnight and the clear liquid syphoned off. The sediment is shaken up with 100 c.c. of hot water and allowed to settle; after removing the clear liquor, the process is repeated with a further quantity of 50 c.c. of hot water. The washed sediment, containing the insoluble barium fluoride, is transferred to a double filter and, when dry, incinerated. The ash is moistened with water, treated with 5 c.c. of concentrated sulphuric acid, and the etching test applied as described on p. 293. It should be noted that many wines contain small traces of fluorides as a natural constituent.

(*c*) *In Beer.*—The following method is given in Allen's

"Commercial Organic Analysis," Vol. I., 1909 ed.: 100 c.c. of the sample are made slightly alkaline with ammonium carbonate, boiled, treated with 2 to 3 c.c. of a 10 per cent. calcium chloride solution and boiled again for 5 minutes. The precipitate is filtered off, washed, dried and tested for fluoride in the usual way.

*Detection and Estimation of Chlorides and Nitrates in Meat.*—The following method, partly due to Given, is described by Leffmann and Beam in their "Food Analysis": It will be necessary first to determine the chlorides present, as these interfere with the nitrate determination; this may be done by titrating the solution obtained by extracting 1 gram of the minced meat with 200 c.c. of water, with decinormal silver nitrate solution, using potassium chromate as indicator; the method of titration is described in most works on quantitative inorganic analysis.

For the determination of nitrates, 1 gram of the sample is placed in a 100 c.c. flask, 50 c.c. of water are added, and the mixture warmed in hot water for 20 minutes, with occasional shaking. For each 1 per cent. of sodium chloride found to be present, 3 c.c. of a saturated solution of silver sulphate are added, then 10 c.c. of basic lead acetate, and 5 c.c. of alumina cream (see p. 226), shaking after each addition. The liquid is made up to 100 c.c., shaken, filtered through a dry fluted filter, the filtrate being returned till clear. 20 c.c. of the filtrate are evaporated to dryness on the water bath in a porcelain dish, and the residue is mixed with 1 c.c. of phenol disulphonic acid, the preparation of which is described below; without applying heat, the acid is stirred over the whole residue; the mixture is completely transferred to a Nessler tube by rinsing with water, and the solution thus obtained made alkaline with ammonia

or soda. By the interaction of the nitrate, the phenol disulphonic acid and the alkali, an alkaline picrate is formed, the depth in colour due to the latter being proportional to the amount of nitrate present in the sample. The determination may therefore be made by comparison with a solution which has been similarly prepared by evaporating to dryness on the water bath a known volume, say, 1 c.c., of a standard solution of potassium nitrate, containing 0·001 gram of the salt per cubic centimetre, treating with phenol disulphonic acid, transferring to a Nessler tube by means of water and rendering alkaline as before. The two picrate solutions are made up to the same volume and compared. If the difference in the depth of colour is not great, some of the deeper coloured solution may be poured off till the tints observed in the two tubes when placed side by side on a white surface are sensibly equal. The relative depths of the two layers of liquid may then be taken as a basis for calculation. If, on the other hand, the difference in tints is very marked, another solution for comparison must be made from a greater or smaller quantity of potassium nitrate.

The phenol disulphonic acid is prepared as follows: 37 grams of pure sulphuric acid and 3 grams of pure phenol are heated for 6 hours in a flask immersed in boiling water. The resulting reagent may crystallise on cooling, but can easily be liquefied on gentle warming.

*Detection and Estimation of Salicylic and Benzoic Acids.*—The following method is recommended by Harry and Mummery for the detection and estimation of salicylic acid in wine and beer; it has the advantage of eliminating tannins which may mask the reaction of salicylic acid with ferric salts, and also substances which tend to give rise to emulsions on extracting with immiscible

solvents. It may equally well be applied to solid or semi-solid foods, in which case it will be necessary to make either an aqueous solution or a slightly alkaline aqueous extract. As far as the actual extraction of the preservative from the sample is concerned, the method is also applicable to benzoic acid.

100 c.c. of the sample (or aqueous solution or extract) are made alkaline with 5 c.c. of normal sodium hydroxide solution, and the alcohol (if any) is driven off at a temperature just below the boiling point. The following operations, up to the ether extraction, have for their object the removal of tannins and pectinous or albuminous matter from the aqueous solution of the preservative. 5 c.c. of normal hydrochloric acid are added, and then 20 c.c. of basic lead acetate solution; the mixture is made alkaline with about 20 c.c. of normal sodium hydroxide solution, and made up to 200 c.c. with water. The tannins are precipitated while the lead salicylate (or benzoate) is soluble in the alkaline solution. After mixing, heating in boiling water and cooling, the liquid is filtered through a dry filter; 100 c.c. of the filtrate are acidified with hydrochloric acid, which will precipitate albuminous matter together with lead chloride, besides liberating the salicylic (or benzoic) acid. The filtrate and washings from the last precipitation are extracted three times with ether, the ethereal extracts united and evaporated to dryness. The identification of salicylic or benzoic acids may be carried out by the methods already described (see p. 289 and below). For the estimation of salicylic acid, Harry and Mummery recommend the following method: The acid is dissolved in a small quantity of dilute alcohol and made up to 100 c.c. in a Nessler tube. The colour produced with ferric chloride solution is then compared with the colour

produced on adding an equal amount of ferric chloride to solutions of the same volume in Nessler tubes containing known amounts of salicylic acid.

In the presence of both benzoic and salicylic acids, van der Laan and Tydens recommend the following method for their separation: After estimating the salicylic acid colorimetrically (see above) in a portion of the aqueous solution, the rest of the solution is extracted with ether, the acids obtained by evaporation of the ethereal extract are dissolved in 10 to 20 c.c. of quarter-normal caustic alkali solution, and a slight excess of a 5 per cent. potassium permanganate solution is added. After gentle heating by means of a small flame, the excess of permanganate and the separated manganic hydroxide are reduced by adding a saturated solution of sulphur dioxide. The salicylic acid will be destroyed by the oxidising agent, while the benzoic acid will remain unaffected. The acidified solution may then be extracted with ether, and the benzoic acid thus obtained identified, and estimated by titration. For the method of separating salicylic and benzoic acids from saccharine, which may mask the reactions for the identification of the former, see below.

*Detection and Estimation of Saccharine in Beverages.*—Saccharine, or ortho-benzoyl-sulphone-imide, or its sodium salt, is not a preservative in the true sense of the word; it is added to beverages in place of sugar, so as to reduce fermentation.

The imide is removed on extracting the acidified material with ether, and may be detected by the sweet taste of the residue obtained on evaporation of the ether. If present together with benzoic and salicylic acids, it will generally accompany these if they are extracted from the material by means of organic solvents. Separa-

tion may be accomplished by acidifying 200 grams of the sample with 5 c.c. of a 20 per cent. phosphoric acid solution, and distilling almost to dryness ; the acids will be found in the distillate, from which they may be obtained by acidifying and extracting with ether, while the saccharine will remain in the flask, and may be obtained by extracting the contents with water and extracting the acid solution thus obtained with ether in the usual way.

Allen's process for the estimation of saccharine in beer is as follows : The beer is concentrated to one-third of its original bulk, and if not acid, it is rendered so by the addition of a little pure phosphoric acid. The liquid is extracted with ether, the latter evaporated, and the residue mixed with an excess of anhydrous sodium carbonate and a little potassium nitrate, and ignited till all organic matter has been burnt off. A determination of sulphate in the residue is made by dissolving in water, acidifying with hydrochloric acid, adding barium chloride solution, etc., as usual. The factor for calculating the barium sulphate to saccharine is 0·785. Care should be taken that the reagents employed are free from sulphur compounds.

*Detection and Estimation of Formic Acid.*—This preservative is chiefly used for fruit juices and preserves. In honey it is present as a natural constituent in quantities up to 0·21 per cent.

According to Croner and Seligmann, formic acid is separated from the sample by mixing 100 grams of the latter with 400 c.c. of water, acidifying with phosphoric acid and distilling in steam. 500 c.c. of distillate are collected, sufficient caustic soda solution being placed in the receiver to keep the whole alkaline. The alkaline distillate is evaporated to 10 c.c., treated with an excess

of baryta solution and filtered; the excess of baryta is then precipitated as sulphate by the addition of sulphuric acid, and the liquid again filtered. By this treatment, acids other than formic acid, which might mask the reactions for the latter, are removed. The filtrate is boiled with mercuric chloride solution, when in the presence of formic acid, a precipitate of mercurous chloride will be produced. According to Smith, formic acid may be identified by adding to the acid steam distillate a slight excess of ammonia above that required for neutralisation, evaporating to a small bulk and adding a few drops of neutral ferric chloride solution; in the presence of formic or acetic acids, a red coloration will be produced; on shaking with 96 per cent. alcohol, a precipitate will be produced in the presence of formic acid, but not in the presence of acetic acid only. An excess of acetic acid interferes with the reaction; in such a case, the acid steam distillate is partially neutralised with about 5 c.c. of normal soda solution, and concentrated to 15 c.c.; most of the formic acid will remain combined with the alkali, while most of the acetic acid will be evaporated off.

H. Fincke recommends the following method for the estimation of formic acid: To the neutral or faintly acid steam distillate containing all the formic acid, obtained as described above (see also below), are added 3 to 5 grams of sodium acetate and at least 15 times as much mercuric chloride (in solution), by weight, as there is formic acid present. The mixture is heated for 2 hours in a flask fitted by means of a rubber stopper with a tube condenser, immersed in boiling water so that the latter reaches to the level of the liquid in the flask. The mercuric chloride solution is prepared by dissolving 100 grams of mercuric chloride and 30 grams of sodium chloride in 100 c.c. of water. The precipitated mer-

curous chloride is filtered off on a Gooch crucible, washed with hot water, alcohol and ether, dried and weighed. The factor for converting mercurous chloride into formic acid is 0·0977.

As regards the steam distillation, it will be necessary to distil at least 500 c.c., in order to bring practically all the formic acid over. As the estimation of the formic acid depends on the reducing action of the steam distillate, errors may be introduced through the presence of volatile aldehydes, which may exist as such in the sample or be produced from tartaric and other acids. To obviate this, the steam may be led through two flasks containing a suspension of calcium carbonate, before it enters the condenser; if the flasks are kept heated, the aldehydes will pass on with the steam, while the formic acid is retained in the flasks as calcium formate. After filtering off the calcium carbonate and washing with water, the formic acid is estimated in the filtrate as described above. Care should be taken to avoid spray being carried over in the distillation, as reducing sugars may be present in the sample, and these would vitiate the result by reducing some of the mercuric chloride. If sulphurous acid is present, the concentrated neutral distillate, or the filtrate from the calcium carbonate, is treated with about 5 c.c. of quarter-normal caustic soda solution and 5 c.c. of concentrated hydrogen peroxide solution, and left for 4 hours; the sulphite will then be oxidised to sulphate. A little freshly precipitated mercuric oxide, made into a paste with water, is then added, and after half an hour the liquid is filtered, and the formic acid estimated in the filtrate as described above. In the presence of salicylic acid, common salt should be dissolved in the distillate; the salicylic acid will then have no influence on the estimation.

*Other Preservatives.*—The detection and estimation of most of the commonly occurring preservatives have been described. One or two methods for detecting a few other substances which may be used as preservatives are briefly outlined below :—

For the detection of $\beta$ naphthol and other similar substances the American Association of Official Agricultural Chemists recommend that 200 grams of the acidified sample be distilled in steam, and the first 200 c.c. of the distillate extracted with 20 c.c. of chloroform ; on separating the latter, rendering it alkaline with caustic potash and heating almost to boiling for a few minutes, colour changes will occur as follows : in the presence of phenol, light red to brown, to yellow, to colourless. In the presence of salol, light red, and in the presence of $\beta$ naphthol, deep blue to green, to brown.

## Part II.—Artificial Colouring Matters.

### Introductory.

The colouring matters used in foods may be classed under three headings : coal-tar dyes, naturally occurring organic colours, and metallic or inorganic colours. The most frequently used are the coal-tar dyes, the majority of which are generally held to be harmless, especially in the small amounts in which they are used, provided, of course, that they are pure, and free from arsenic. The great majority of the vegetable colouring matters are also harmless, but the metallic colouring matters, such as chromates, copper salts, etc., are mostly injurious, even in small amounts. The vegetable colouring matters such as cochineal, anatto, turmeric and saffron, have largely been superseded by the coal-tar colours, while mineral colours, with the exception, perhaps, of copper sulphate, are of comparatively rare occurrence in foods. Among the few poisonous organic colours may be mentioned gamboge and picric acid.

The law of the United Kingdom does not definitely forbid the use of colouring matters in any food, or limit the amounts in which they may be used; as in the case of preservatives the addition of any objectionable colouring matter would, in all probability, be dealt with under section 6 of the Sale of Foods and Drugs Act of 1875 (see p. 282). Even when the colouring matter itself is harmless, its presence would be objectionable if it had been added in order to conceal the inferior quality of the food, as might be done, for example, in the case of meat, milk or wine.

The Departmental Committee on Preservatives and Colouring Matters in Foods, 1901, recommended that the use of colouring matters of any kind in milk offered for sale in the United Kingdom should be considered an offence under the Sale of Foods and Drugs Act. Further, that the use of copper salts in the so-called greening of preserved foods should be prohibited. These recommendations have, however, not resulted in any legislation on the subject.

The use of copper salts in foods is prohibited in Germany and Austria-Hungary. In the United States certain specified colouring matters only are allowed in foods, pending further enquiry. Copper salts are not prohibited, but their presence must be notified.

The identification of organic colouring matters, especially coal-tar dyes, in foods, may often be a difficult task, requiring considerable experience. In many cases the full identification of the colouring matter will not be necessary; it will be sufficient to determine its nature, and to be able to say whether it is harmless or injurious. By the methods given below, the general nature of the colouring matter present may be determined; the methods for the detection of some of the commoner vegetable colouring matters are also given.

*Dyeing Method for the Detection of Coal-tar Colours.*— The method described is recommended by Thresh and Porter ("Preservatives in Food and Food Examination") for the detection of both acid and basic coal-

tar dyes, being based on the method of Sostegni and Carpenteri for the detection of acid dyes. It may generally be employed for the detection of coal-tar dyes[1] in meat, wine, confectionery, milk, fruit juices and extracts, etc.

The majority of the dyes found in foods are of an acid nature, only few basic colours being met with. If clean white wool is immersed in an acid solution of an acid dye, or an alkaline solution of a basic dye, it will take up the colour in both cases, forming insoluble compounds with dyes of both classes, presumably owing to its containing both basic and acid constituents. In addition to coal-tar colours, the wool will take up some vegetable colours, such as cochineal or logwood ; if, however, the acid dye, for example, be dissolved from the wool by means of an alkaline solution, then, on acidification of the latter, a second piece of wool may be dyed from it if a coal-tar colour be present, but not if the first dyeing was due to a vegetable colour. The same holds good, *mutatis mutandis*, as regards basic dyes.

In the first place, it will be necessary to prepare a clear solution or extract of the material containing the colour. Solid material should be broken up by passing through a sausage grinder, when the colour may be extracted by warming with water or 80 per cent. alcohol. The filtered solution of the colour is divided into two portions of 50 to 100 c.c. each, the one of which is rendered faintly alkaline with ammonia, and the other distinctly acid with hydrochloric acid. Into each of these solutions is put about a foot of white worsted which has previously been boiled in a very dilute solution of caustic soda in distilled water, and washed till free from alkali. The solutions are kept at the boiling point for

[1] See also p. 315.

an hour, or less if the wool in one of them is distinctly dyed. The dyed wool is removed, pressed between sheets of filter paper, and washed by immersing in two successive portions of 20 c.c. of boiling water.

The wool, if dyed from the acid solution, is then immersed in about 20 c.c. of a boiling solution of dilute ammonia containing 10 per cent. by volume of the concentrated ammonia of specific gravity 0·880, or, if dyed from the alkaline solution, in the same quantity of boiling 5 per cent. acetic acid. The wools are removed, and the alkaline liquid made acid by the addition of acetic acid, and the acid liquid made alkaline by ammonia. A fresh piece of white, grease-free worsted, about 2 to 3 inches long, is placed in each solution; after heating for half an hour on a boiling-water bath, the wools are removed and washed in distilled water; if a coal-tar dye was present in the original solution, one of the samples should be brilliantly dyed; if the dye present is basic, the most distinct dyeing will take place from the alkaline solutions, if acid, from the acid solutions. In presence of vegetable colours, the second piece of worsted will acquire, at most, a dirty appearance.

For identification, the colour may be removed from the wool used in a first dyeing, as described above, either by means of acid or alkali, and the tests applied to the solution. The identification of coal-tar colours may be a difficult task, requiring some special experience; the subject is fully dealt with in Vol. V. of Allen's "Commercial Organic Analysis," where several recognised schemes are given; the other works mentioned at the end of this chapter may also be consulted.

*Colouring Matters in Milk.*—According to Wynter Blyth, the addition of colours to milk is frequently practised in the United Kingdom, the chief colours used

being sulphonated azo-dyes and añatto; other colours said to have been used are turmeric, saffron, carrot, marigold and chromates.

Coal-tar colours will usually be detected in milk by the dyeing test given above, though complications may sometimes occur owing to the separation of the colour with the curd on acidification. The following method for separating the colours most likely to occur in milk, and tests for their identification, recommended by Wynter Blyth, may be applied with advantage:—

If the fresh milk gives a pink colour with hydrochloric acid, the presence of a sulphonated azo-dye may be inferred.

If a piece of filter paper soaked for 24 hours in the milk, previously make alkaline with sodium carbonate, takes a brown stain which is changed to pink by hydrochloric acid, the presence of anatto may be inferred.

To test for caramel, 10 c.c. of the milk are coagulated by acetic acid, and the curd is collected by straining through linen, transferred to a white porcelain dish and just covered with concentrated hydrochloric acid; a control sample, known to be free from caramel, is treated in the same manner. A blue violet coloration on adding the acid to the curd in the dish indicates the presence of caramel.

For the isolation of the various classes of colouring matters, for the application of special tests, the following method is recommended: At least 60 c.c. of milk are made just alkaline to delicate litmus paper by the addition of dilute soda or strontia solution, and evaporated to a thin paste on the water bath. The paste is thoroughly extracted with ether, which will remove the fat and, if the milk is sour, the products of those dyes which have been reduced by nascent hydrogen produced

by certain bacteria (compare Reductase Test, p. 218). The ether is evaporated off, and the fat shaken with warm water. The water is separated and evaporated to dryness in a white porcelain dish; a coloured residue will be due to added colour, which may possibly be identified by the special tests given in Wynter Blyth's "Foods: Their Composition and Analysis," 1909, p. 242.

The fat-free residue is extracted with boiling alcohol, which is filtered and evaporated to dryness in a white porcelain dish. If the residue is yellow or orange, a portion of it is taken up with a little decinormal acid, and shaken with ether. In the presence of the following dyes, the ether will be coloured: natural colours, such as anatto, saffron, turmeric, etc., and acid coal-tar dyes, including the acid azo-dyes, but not the sulphonated azo-dyes. The latter, as well as the basic dyes, do not colour the ether.

Coal-tar dyes may be recognised by the dyeing test described above, either in the aqueous layer, or in an aqueous solution of the residue obtained by evaporating the ethereal layer to dryness. In the latter it will not be necessary to look for basic dyes, but in the former either acid or basic dyes may be found.

Wynter Blyth recommends the following tests for anatto in the residue obtained by evaporating the ethereal layer, as supplementary to the preliminary test described above: (i.) A drop of the colouring matter dissolved in water and made alkaline with potash gives an orange stain on filter paper, which is changed to pink by stannous chloride solution. (ii.) A little of the colouring matter is dissolved in water containing a little alcohol and a drop of ammonia; a bundle of white cotton fibres is introduced, and the liquid evaporated nearly to dryness. The fibre is then immersed in a solution of

citric acid; it will be coloured rose red if anatto is present.

*Colouring Matters in Meat.*—Meat is generally coloured with coal-tar dyes, such as fuschine, eosin and benzopurpurin. These may be recognised by extracting with alcohol, and applying the dyeing test to the extract as described above. Carmine and cochineal have also been used for colouring meat.

The following method, due to Klinger and Bujard, and modified by Bremer, may be used for the detection of carmine: 20 grams of the minced meat are heated on the water bath for several hours with a mixture of equal parts of glycerol and water which has been slightly acidulated with tartaric acid; the liquid is separated by straining through muslin, and when cold, filtered in order to separate it from fat and suspended matter. On adding alum solution and then ammonia, the precipitated aluminium hydroxide will carry the colour with it, as a lake; the latter is filtered off, washed with water, dissolved in a small quantity of tartaric acid solution, and examined in the spectroscope; if carmine is present the solution will show absorption bands at *b* and E, and another close to D, in the solar spectrum.

*Colouring Matters in Wine.*—Coal-tar dyes will be detected by the dyeing test, described above; in addition to these, such materials as elderberry, logwood and cochineal are said to be in use for colouring wine. The subject is fully treated of in Wynter Blyth's "Foods: Their Composition and Analysis," as well as in some of the other works mentioned at the end of this chapter. The tests used at the Municipal Laboratory of Paris for detecting artificial colouring matters in wine are given on p. 458 of the above-mentioned work (1909 edition).

*Detection and Estimation of Metallic Colouring Matters.*

—The commonest metallic colouring matter used in foods is, perhaps, copper sulphate, which is added to preserved peas, spinach, etc., to impart a bright green colour and, at the same time, to harden the integument.

A general method for the detection of compounds of copper, arsenic, lead, chromium, zinc, etc., all of which must be regarded as poisonous, is as follows : A known weight, say 100 grams of the material, in the case of preserved vegetables or fruits, strained before weighing, is burnt off at a low red heat, the residue moistened with concentrated hydrochloric acid, and heated with a little water on a boiling-water bath ; after filtering and washing, the insoluble residue is thoroughly incinerated at a bright red heat, dissolved in dilute hydrochloric acid, and the solution added to the filtrate obtained from the previous operation. The metals may then be detected and estimated in the solution by the ordinary methods of inorganic analysis. The heating of the material should be carried out in a porcelain, and not in a platinum dish, as the latter may be attacked by the foreign metals present.

Arsenic, if present, will usually have been introduced as an impurity with organic or mineral colouring matters, or other materials used in the manufacture or preparation of the food, and is, therefore, only likely to be present in very small amounts ; and must accordingly be tested for in the original material by special methods, such as the Marsh test ; methods for the detection of arsenic in foods will be found fully described in Wynter Blyth's "Foods : Their Composition and Analysis," and some of the other works mentioned at the end of this chapter.

Ferric oxide is said to be added to cocoa, in order to improve its colour, and as an adulterant ; it may be detected and estimated on the same lines as described above for other mineral additions to foods.

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